DOCUMENT RESUME

ED 207 790 SE 033 651

AUTHOR Ballinger, Jack T.; Wolf, Lawrence J.
TITLE Chemical Science and Technology II. A Study Guide of the Science and Engineering Technician Curriculum.
INSTITUTION Saint Louis Community Coll. at Florissant Valley, Mo.
SPONS AGENCY National Science Foundation, Washington, D.C.
PUB DATE 76
GRANT NSF-GZ-3378; NSF-HES74-22284-A01; NSF-SED77-17935
NOTE 65p.; For related documents, see SE 033 647-657. Not available in paper copy due to copyright restrictions. Contains occasional light and broken type.
AVAILABLE FROM National Science Teachers Association, 1742 Connecticut Ave., N.W., Washington, DC 20009 (write for correct price).

EDRS PRICE MF01 Plus Postage. PC Not Available from EDRS.
DESCRIPTORS Chemical Reactions; *Chemistry; College Science; Engineering Education; Higher Education; Instructional Materials; Organic Chemistry; Plastics; *Science Course Improvement Projects; Science Curriculum; Science Education; Science Instruction; *Study Guides; *Technical Education; Two Year Colleges
IDENTIFIERS *Science and Engineering Technician Curriculum

ABSTRACT

This study guide is part of a program of studies entitled the Science and Engineering Technician (SET) Curriculum developed to provide a framework for training technicians in the use of electronic instruments and their applications. This interdisciplinary course of study integrates elements from the disciplines of chemistry, physics, mathematics, mechanical technology, and electronic technology. This guide provides the content for the chemistry component of the curriculum including: (1) solutions and concentrations; (2) chemical equations; (3) electrochemistry; (4) gas laws; and (5) organic materials. (Author/SK)

****
* Reproductions supplied by EDRS are the best that can be made *
* from the original document. *
****

ED207790

U.S. DEPARTMENT OF EDUCATION
NATIONAL INSTITUTE OF EDUCATION
EDUCATIONAL RESOURCES INFORMATION CENTER (ERIC)

X This document has been reproduced as received from the person or organization originating it.

☐ Minor changes have been made to improve reproduction quality.

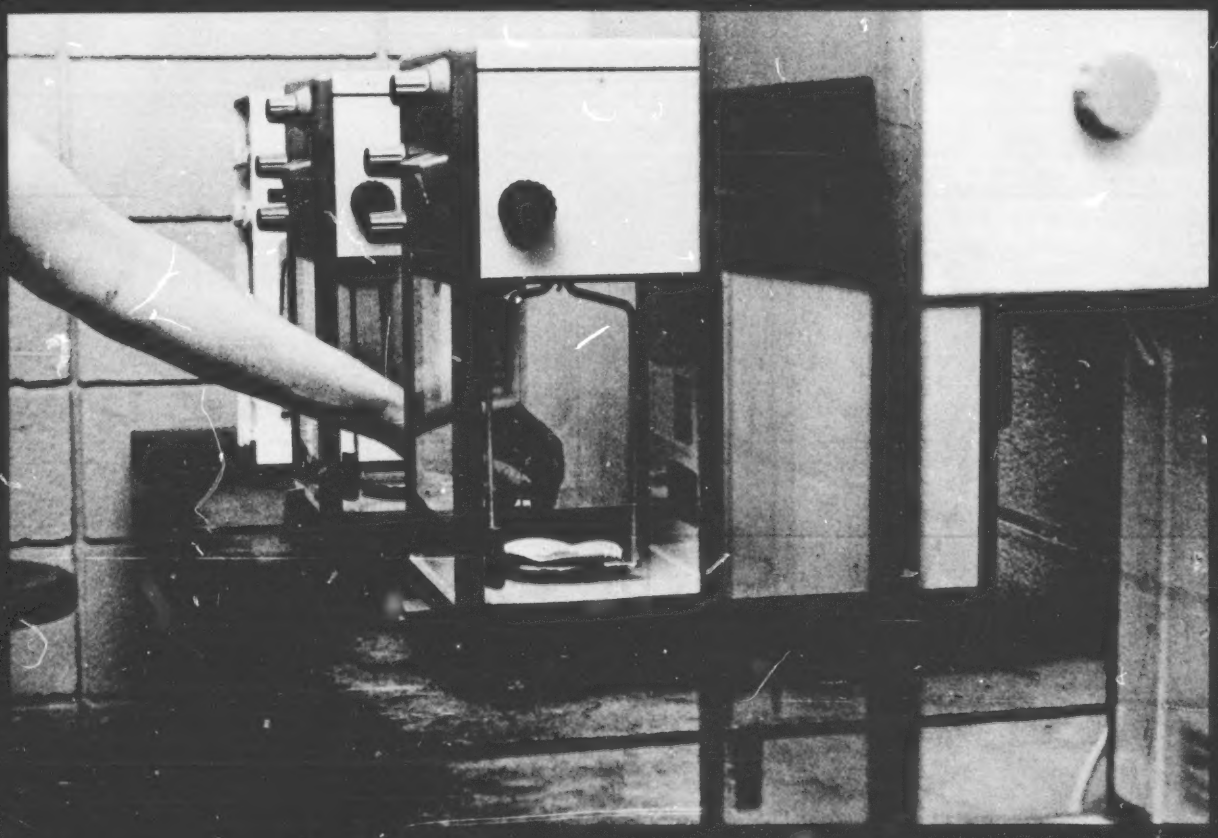
• Points of view or opinions stated in this document do not necessarily represent official NIE position or policy.

"PERMISSION TO REPRODUCE THIS MATERIAL IN MICROFICHE ONLY HAS BEEN GRANTED BY

Patricia Babb
Bill Aldridge

TO THE EDUCATIONAL RESOURCES INFORMATION CENTER (ERIC)."

CHEMICAL SCIENCE AND TECHNOLOGY II



A study guide of the Science and Engineering Technician Curriculum

Developed under a grant from the National Science Foundation

SE 033 651

SEDR DATA FORMAT	1. Award Number	2. Award Date	3. Termination Date
	SED77-17935	September 28, 1977	July 31, 1979

6. Title
Chemical Science and Technology II:
A Study Guide of the Science and Engineering Technician Curriculum

4. Amount of Award
$70,400 (Cum. Amt.)

5. Type
Final Tech. Report

7. Performing Organization
SET Project
St. Louis Community College at Florissant Valley
St. Louis, MO 63135

8. Pagination
62 pages

9. Accession Number
00320

11. Principal Investigator: Field or Specialty
Donald R. Mowery
Lawrence J. Wolf
Bill G. Aldridge

10. Performing Organization Report Number

12. NSF Program Manager
Gene D'Amour

13. SEDR Program
DISE

14. SEDR Subprogram

15. Abstract

This study guide is part of a program of studies entitled the Science and Engineering Technician Curriculum (SET). This interdisciplinary course of study integrates elements from the disciplines of chemistry, physics, mathematics, mechanical technology, and electronic technology. The objective of this national curriculum development project was to provide a framework for training technicians in the use of electronic instruments and their applications.

Two guides, Chemical Science and Technology I and II, provide the content for the chemistry component of of the curriculum. This volume includes the following topics: (1) solutions and concentrations, (2) chemical equations, (3) electrochemistry, (4) gas laws, and (5) organic materials.

16. Descriptors

Study Guides
Instructional Materials
Associate Degrees
Engineering Technology
Technical Education
Chemistry
Chemistry Instruction
Science Curriculum

17. Identifiers
Science and Engineering Technician Curriculum (SET)

18. Field
Engineering Education
Chemistry, General

19. Target Audience
Two-Year College Students

20. Availability
Limited number of copies available from St. Louis Community College at Florissant Valley, St. Louis, MO 63135

21. Supplemental Notes
One copy

CHEMICAL SCIENCE AND TECHNOLOGY II

A Study Guide of The Science and Engineering Technician Curriculum

Authors: Jack T. Ballinger
St. Louis Community College at Florissant Valley

Lawrence J. Wolf
St. Louis Community College at Florissant Valley

Project Directors: Bill G. Aldridge
Donald R. Mowery
Lawrence J. Wolf

Study Guide Editor: Peggy Dixon
Montgomery College, Takoma Park, MD

Address: SET Project
St. Louis Community College at Florissant Valley
St. Louis, Missouri 63135

Copyright © 1976 by St. Louis Community College at Florissant Valley. Printed in the United States of America. All rights reserved. This book or parts thereof may not be reproduced in any form without permission.

The materials contained herein were developed under Grant Numbers HES74-22284 A01, GZ-3378, and SED77-17935.

TABLE OF CONTENTS

	Page
CHAPTER I - SOLUTIONS AND CONCENTRATIONS.	1
Section 1 - Concentration Expressions.	1
Section 2 - pH	5
CHAPTER II - CHEMICAL EQUATIONS	8
Section 1 - Balancing Chemical Equations	8
Section 2 - Stoichiometry.	13
Section 3 - Theoretical and Actual Yields.	14
Section 4 - Limiting Reagent	16
CHAPTER III - ELECTROCHEMISTRY.	19
Section 1 - The Galvanic Cell.	19
Section 2 - The Corrosion of Iron and Steel.	22
Section 3 - Galvanic Corrosion	23
Section 4 - Applied Electrochemistry	28
Section 5 - Corrosion Control and Prevention	34
CHAPTER IV - GAS LAWS , ...	36
Section 1 - Gas Pressure	36
Section 2 - The Ideal Gas Law.	38
CHAPTER V - ORGANIC MATERIALS	45
Section 1 - Chemistry of Plastics.	45
Section 2 - Selection of Plastics.	51
Section 3 - Elastomers	53
Section 4 - Adhesives.	56
INDEX	58

DEC 1 2 1980

Chapter I

Solutions and Concentrations

SECTION 1: CONCENTRATION EXPRESSIONS

A solution is a homogeneous (uniform) mixture of two or more substances. The solvent is the component (usually in relatively large proportion) that does the dissolving, while the solute is present in smaller proportion and is said to be dissolved. The solution is both the solvent and solute combined. Two terms are continually used in discussing concentrations but are poorly defined: dilute, indicating a small amount of solute and concentrated indicating a large amount of solute.

Some familiar examples of solutions are: sugar in water, carbon dioxide gas in water (club soda), alcohol in water (vodka), iodine in alcohol (tincture of iodine) and oxygen in helium. In the example of sugar in water, it is clear that sugar is the solute while water is the solvent. This is not as clear for mixtures of water and alcohol. For a wine that contains 20% alcohol in water, it may be assumed that alcohol is the solute but not true for vodka that contains 40% alcohol. In some special cases, the solution can be a solid as in the case of metal alloys (e.g. brass, bronze, solder, etc.).

Chemical Concentration Expressions

a. The percent of solute by mass is a common quantitative expression.

$$\text{Mass percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

Example: The mass percent of 15 grams of sucrose dissolved in 85 grams of water is

$$\frac{15\ g}{15\ g + 85\ g} \times 100 = 15\% \text{ sucrose}$$

An alloy is a solution of two or more elements (usually metals) blended to possess certain chemical and physical properties.

Composition of Some Common Alloys

Trade Name	Composition, % by Weight
Dentist Amalgam	50 Hg, 35 Ag, 13 Sn, 1.5 Cu, 0.5 Zn
Sterling Silver	92.5 Ag, 7.5 Cu
18 Carat Yellow Gold	75 Au, 12.5 Ag, 12.5 Cu
18 Carat White Gold	75 Au, 3.5 Cu, 16.5 Ni, 5 Zn
Bronze	70-95 Cu, 1-25 Zn, 1-18 Sn
Stainless Steel	73-79 Fe, 14-18 Cr, 7-9 Ni
Invar	64 Fe, 36 Ni

b. Parts per million (ppm) concentration units are usually used to express very low percent concentrations; this avoids the use of very small numbers. For example, the parts per million (ppm) of carbon dioxide normally found in the air is 300. The percent CO_2 in the atmosphere would be 10,000 times less or 0.0300%. Note that ppm = % x 10^4.

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

Example: 0.0123 grams of DDT were found in 1000 grams of Mississippi River water. Calculate the ppm DDT.

$$\text{ppm} = \frac{0.0123 \text{ g}}{1000 \text{ g}} \times 10^6 = 12.3 \text{ ppm DDT}$$

c. Mole fraction expressions are used in situations where the ratio of solute molecules to solution molecules is important (gas law calculations, for example).

$$\text{mole fraction A} = \frac{\text{moles of A}}{\text{moles of A + moles of all other components}}$$

Example: Calculate the mole fraction of 46 g ethanol (C_2H_5OH; molecular weight = 46) in a solution of 36 g water (H_2O; molecular weight = 18)

$$\text{mole fraction, ethanol} = \frac{1 \text{ mole}}{1 \text{ mole} + 2 \text{ moles}} = \frac{1}{3} = 0.33$$

d. Molality is a concentration expression which uses moles of solute for a given mass of solvent in kilograms. The symbol for molality is m.

$$\text{molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

Example: If 36 grams of glucose (0.200 mole) are dissolved in 600 grams H_2O (0.600 kg), the molality is:

$$m = \frac{0.200 \text{ mole}}{0.600 \text{ kg}} = 0.33$$

e. Molarity is the expression of concentration most frequently used in a chemistry laboratory. This system is convenient because volume measurements are generally more convenient than mass measurements in the laboratory. The symbol for molarity is M.

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Example: If 36 grams of glucose (0.200 mole) are dissolved in enough water to make 600 ml (0.600 ℓ), the molarity of glucose is:

$$M = \frac{0.200 \text{ mole}}{0.600 \text{ liter}} = 0.333$$

f. The normality of a solution is the number of gram equivalent weights per liter of solution. The symbol for normality is N.

$$N = \frac{\#GEW}{\text{liters of solution}}$$

To make the concept of GEW broad enough to encompass solutions of all types of solutes, it is defined as the gram molecular weight divided by the "combining capacity," n_c, of the solute:

$$GEW = \frac{GMW}{n_c}$$

Thus:

$$N = n_c M$$

The combining capacity of a substance depends on the reaction for which it is to be used. In general, we may make the following assumptions:

acids n_c = number of reactive hydrogens per formula {usually x for acid of type H_xY}

bases n_c = number of reactive OH^- ions per formula {x for base of type $M(OH)_x$}

salts n_c = total number of positive or negative charges per formula

oxidizing or reducing agents n_c = number of electrons gained or lost per formula

Examples: What is the normality of a 0.500 M H_2SO_4 solution? Since H_2SO_4 is acting as an acid, n_c = 2 active hydrogens.

$$N = n_c M$$

$$= (2 \text{ GEW/mole})(0.500 \text{ mole/liter})$$

$$= 1.00 \text{ GEW/liter}$$

or $\boxed{1.00 \text{ N}}$

Calculate the GEW of H_3PO_4:

$$GEW = GMW/n_c = \frac{98.0 \text{ g/mole}}{3 \text{ GEW/mole}^*}$$

$$= \boxed{32.7 \text{ g/GEW}}$$

* Note: Assuming that the H_3PO_4 reacts with all three hydrogens.

WORKED EXAMPLES

1. Explain how you would prepare 200 ml of an aqueous solution of NaCl containing 0.040 g NaCl per ml.

   Each ml of solution contains 0.040 g NaCl. Therefore, 200 ml of solution will contain 0.040 g/ml x 200 ml = 8 g NaCl. Dissolve 8 g NaCl in about 150 ml water. Then add sufficient water to make the volume exactly 200 ml.

2. Calculate the weight of anhydrous HCl in 10.00 ml of concentrated hydrochloric acid of density 1.17 and containing 37% HCl by weight.

   One ml of solution weighs 1.17 g. Weight of 10.00 ml = 10.00 ml x 1.17 g/ml = 11.70 g. Since the solution contains 37.0% HCl by weight, the weight of HCl in the 11.70 g solution = 0.37 x 11.70 g = 4.33 g anhydrous HCl.

3. A solution of ammonia contains 29.0% NH_3 by mass and has a density of 0.899 g/ml. Calculate the mass of ammonia in 100.0 ml of the solution.

   mass solution = volume solution x density solution
   mass solution = 100 ml x 0.899 g/ml
   = 89.9 g

$$\text{mass percent } NH_3 = \frac{\text{mass } NH_3}{\text{mass solution}} \times 100$$

$$\text{mass } NH_3 = \frac{\text{mass percent } NH_3}{100} \times \text{mass solution}$$

$$\text{mass } NH_3 = \frac{29.0}{100} \times 89.9 \text{ g} = 26.1 \text{ g } NH_3$$

4. Calculate the molality and molarity of ammonia (NH_3) in the solution in Problem 3.

   Problem 3 showed that there are 26.1 g NH_3 in 100 ml of 29.0% NH_3, whose density is 0.899 g/ml (molecular weight NH_3 = 17.0).

$$\text{moles } NH_3 = \frac{\text{mass } NH_3}{17.0 \text{ g } NH_3/\text{mole}} = \frac{26.1 \text{ g}}{17.0 \text{ g/mole } NH_3} = 1.54 \text{ moles } NH_3$$

   The mass of the solution from Problem 3 is 89.9 g. Since 26.1 g of this mass is due to NH_3, the remainder (89.9 g - 26.1 g = 63.8 g or 0.0638 kg) is water.

$$\text{molality } NH_3 = \frac{\text{moles } NH_3}{\text{kg water}} = \frac{1.54 \text{ moles}}{0.0638 \text{ kg}} = 24.1 \text{ m}$$

$$\text{molarity } NH_3 = \frac{\text{moles } NH_3}{\text{liter solution}} = \frac{1.54 \text{ moles}}{0.100 \text{ l}} = 15.4 \text{ M}$$

Laboratory

The student should prepare assigned solutions of various concentrations using different types of gravimetric and volumetric equipment (balances, weighing bottles, pipets, burets, etc.)

Student Problems

1. How many moles of $(NH_4)_2SO_4$ are needed to prepare 7.5 liters of 0.30 M $(NH_4)_2SO_4$? (2.25)

2. Find the mass of iodine in 400 g of a 3.0% solution of iodine by mass. (12.0 g)

3. A solution contains 116 g acetone (CH_3COCH_3), 138 g ethanol (C_2H_5OH) and 126 g water. Determine the mole fraction of each compound. (Acetone = 0.167, alcohol = 0.25 water = 0.583)

4. Calculate the normality of a 0.25 M HNO_3 solution. (0.25 N)

5. What is the GEW of $BaCl_2$? (104.12)

6. What normality would a 1.00 M $Ca(OH)_2$ solution be? (2.00 N)

SECTION 2: pH

Water undergoes autoionization to give H+ and OH- ions.

$$H_2O \rightleftarrows H+ + OH-$$

This ionization takes place at room temperature to only a slight extent as shown by this ion product constant (K_w) for water

$$K_w = [H+][OH-] = 1.0 \times 10^{-14}$$

where the [ ] mean concentration is expressed in moles/liter. When H+ or OH- ions are also supplied from some other source, such as addition of an acid or base to the water, the concentration of H+ may exceed the concentration of OH-, or vice versa. In every case, however, the K_w relationship is applicable.

Example: What is the concentration of H+ in an aqueous solution having an OH- concentration of 1.0×10^{-2} M?

$$K_w = [H+][OH-] = 1.0 \times 10^{-14}$$

$$[H+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12} \text{ M}$$

A solution having a hydrogen ion concentration of greater than 10^{-7} M is said to be acidic; one with a H+ concentration of less than 10^{-7} is said to be basic. For convenience the hydrogen ion content of a solution may also be expressed in pH units, where:

$$pH = -\log[H+]$$

Similarly:

$$pOH = -\log[OH-]$$

From the K_w relationship:

$$pH + pOH = 14.00$$

$[H^+]$, moles/liter		$[OH^-]$, moles/l	pH	pOH	
1	$= 10^0$	10^{-14}	0	14	Strongly acidic
0.1	$= 10^{-1}$	10^{-13}	1	13	
0.001	$= 10^{-3}$	10^{-11}	3	11	
0.00001	$= 10^{-5}$	10^{-9}	5	9	Weakly acidic
0.0000001	$= 10^{-7}$	10^{-7}	7	7	Neutral
0.000000001	$= 10^{-9}$	10^{-5}	9	5	Weakly basic
0.00000000001	$= 10^{-11}$	10^{-3}	11	3	
0.00000000000001	$= 10^{-13}$	10^{-1}	13	1	
0.00000000000001	$= 10^{-14}$	1	14	0	Strongly basic

Examples: a) What is the pH of a solution in which the hydrogen ion concentration is 1.0×10^{-5} M?

$$pH = -\log[H+]$$

$$= -\log[1.0 \times 10^{-5}]$$

$$= -(-5)$$

$$= \boxed{5}$$

b) What are the pH and pOH of a solution having a hydrogen ion concentration of 2.5×10^{-6} M?

$$pH = -\log[H+]$$

$$pH = -\log[2.5 \times 10^{-6}]$$

$$pH = 5.6$$

Thus, $pOH = 14.0 - pH$

$pOH = 14.0 - 5.6$

$pOH = 8.4$

11

c) What is the hydrogen ion concentration of a solution with a pH of 1.5?

$pH = -\log[H+]$ or $[H+] = \text{antilog}\ (-pH)$

$[H+] = \text{antilog}\ (-1.5)$

$= 3.2 \times 10^{-2}$ M.

Laboratory

The student should be able to operate a pH meter which would include calibration. The preparation of buffer solutions and proper care of pH electrodes should be included.

Student Problems

1. Calculate the pH of a 1×10^{-3} M HCl solution. (3)
2. Calculate the pH of a 5.4×10^{-9} M HNO_3 solution. (8.27)
3. Change a pH value of 4 to its respective $[H+]$ value. (1×10^{-4} M)
4. Change a pH value of 3.6 to its respective $[H+]$ value. (2.5×10^{-4} M)

Chapter II

Chemical Equations

SECTION 1: BALANCING CHEMICAL EQUATIONS

The Conservation of Matter Law states that matter can neither be created nor destroyed by chemical means. This law can be demonstrated by the chemical equation used to represent the combustion of natural gas (methane).

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O$$

This simple equation is said to be unbalanced since the number of atoms on the reactants (left) side of the equation does not equal the number of atoms on the products (right) side. The reactants side contains 1 carbon, 4 hydrogen, and 2 oxygen atoms while the products side contains 1 carbon, 2 hydrogen, and 3 oxygen atoms. This unbalanced equation can not be true since it violates the Conservation of Matter Law.

To balance a chemical equation, coefficients are used in front of formulas where necessary to produce the same number of atoms on both the left and right sides of the equation (arrow). The balanced equation for the combustion of methane would be:

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$$

In balancing an equation, it is correct to change the coefficients as needed but never change the formulas themselves. For example, if additional hydrogen atoms are needed on the reactant side of the equation, increase the coefficient in front of the CH_4 and not the subscript on the CH_4. A change in the subscript on the CH_4 molecular formula would change the compound itself, thus, creating an entirely new reactant.

Worked Example

Balance the equation:

$$C_3H_8 + O_2 \longrightarrow CO_2 + H_2O$$

(balanced)

$$C_3H_8 + 5\ O_2 \longrightarrow 3\ CO_2 + 4\ H_2O$$

Student Problems

1. Balance the following equations:

a) $HCl + Ba(OH)_2 \longrightarrow BaCl_2 + H_2O$ (2, 1 ⟶ 1, 2)

b) $C_6H_6 + O_2 \longrightarrow CO_2 + H_2O$ (1, 7½ ⟶ 6, 3)

c) $P_4 + O_2 \longrightarrow P_4O_{10}$ (1, 5 ⟶ 1)

Most chemical reactions fall into two categories: (1) displacement, (2) reduction-oxidation. The displacement category includes most acid-base and precipitation reactions in which the oxidation numbers of the participating atoms do not change. In reduction-oxidation (redox) reactions, however, changes in the oxidation numbers of one or more atoms take place.

The oxidation number of an atom is an "arbitrarily" assigned number, usually, but not necessarily, an integer. It may be either positive or negative, except that it is zero for free elements. Roman numerals are normally used to distinguish oxidation numbers from ionic changes and coefficients.

In a redox reaction, the particle (atom or ion) whose oxidation number changes in the positive direction is said to be oxidized. The particle whose oxidation number changes in the negative direction is said to be reduced.

The rules for determining oxidation numbers are as follows:

1. The oxidation number of any free element or of any element combined to itself is zero.

Element	Oxidation Number
Zn	0
O_2	0
Cl_2	0
He	0

2. The oxidation number of hydrogen in a compound is +1, except when it is combined with active metals (Na, Ca, etc.) to form hydrides (NaH, CaH_2, etc.) and becomes -1.

3. The oxidation number of oxygen in a compound is -2, except in peroxides (BaO_2, H_2O_2, etc.) where it is -1.

4. The oxidation number of an ion is the same as the charge on the ion.

Ion	Oxidation Number
$(NO_3)^-$	-1
S^{-2}	-2
$(SO_4)^{-2}$	-2
$(NH_4)^+$	+1

5. The algebraic sum of the oxidation numbers in a molecule is zero.

Molecule	Oxidation Numbers	Algebraic Sum
$CaCl_2$	(Ca = +2, Cl = -1)	(+2, -1, -1) = 0
$HClO_4$	(H = +1, Cl = +7, O = -2)	(+1, +7, -2,-2,-2,-2) = 0
NaClO	(Na = +1, Cl = +1, O = -2)	(+1, +1, -2) = 0

Worked Examples

1. Find the oxidation number of each atom in the following compounds or ions:

a) HCl (H = +1, Cl = -1)

b) SO_3^{-2} (S = +4, O = -2)

c) Cl_2 (Cl = 0)

d) CaH_2 (Ca = +2, H = -1)

2. (a) Classify each of the following reactions as a displacement or redox type.
(b) find the oxidation number of each participant in the reaction, and
(c) indicate which substance is oxidized and which is reduced.

1. $AgNO_3 + HCl \xrightarrow{\nu} AgCl + HNO_3$

a) displacement
b) Ag = +1, N = +5, O = -2, H = +1, Cl = -1
c) N/A

2. $2\ H_2 + O_2 \longrightarrow 2\ H_2O$

a) redox
b) H = 0, O = 0 to H = +1, O = -2
c) H_2 is oxidized and O_2 is reduced

Student Problem

1. (a) Classify each of the following reactions as a displacement or redox type,
(b) find the oxidation number of each participant in the reaction, and
(c) indicate which substance is oxidized and which is reduced.

I. $Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\ H_2O$

II. $H_2 + 3\ N_2 \longrightarrow 2\ NH_3$

III. $2\ Mg + CO_2 \longrightarrow C + 2\ MgO$

Answers

I. a) displacement
b) Ba = +2, O = -2, H = +1, S = +6
c) N/A

II. a) redox
b) H = 0, N = 0 to H = +1, N = -3
c) H_2 is oxidized and N_2 is reduced

III. a) redox
b) Mg = 0, C = +4, O = -2 to C = 0, Mg = +2
c) C is reduced and Mg is oxidized

Balancing redox equations is often more complicated than balancing the displacement type reactions (acid-base or precipitation equations). The ion-electron method is very effective because it separates and later recombines the oxidation reaction and the reduction reaction. However, we will demonstrate the simpler oxidation-number method:

Step 1. Given this word equation:

Iron (III) oxide + carbon ⟶ iron + carbon (IV) oxide

Step 2. Write the symbols for the unbalanced equation:

$Fe_2O_3 + C \longrightarrow Fe + CO_2$

Step 3. Assign the oxidation number of each element in the unbalanced equation:

$$\overset{+3\ -2}{Fe_2O_3} + \overset{0}{C} \longrightarrow \overset{0}{Fe} + \overset{+4-2}{CO_2}$$

Step 4. Determine which elements have undergone a change in oxidation number:

$2\ Fe^{+3} \longrightarrow 2\ Fe^{0}$ a decrease of 6 (reduction)

$C^{0} \longrightarrow C^{+4}$ an increase of 4 (oxidation)

Step 5. Use the numbers found in Step 4 to determine the simplest ratio of moles of Fe^{+3} to moles of C^{0}. This is accomplished by multiplying through by appropriate coefficients so that the decrease in oxidation number for reduction is balanced by the increase in oxidation number for oxidation. Thus,

$2x(2\ Fe^{+3} \longrightarrow 2\ Fe^{0})$ or 2 times decrease of 6 = -12

$3x(\ C^{0} \longrightarrow C^{+4})$ or 3 times increase of 4 = +12

Step 6. The balancing shows 4 moles of Fe^{+3} ($2xFe_z^{+3}$) and 3 moles of C^{0} to be necessary. Thus,

$2\ Fe_2O_3 + 3\ C \longrightarrow 4\ Fe + 3\ CO_2$

Student Problems

1. Using the oxidation number method, balance the following redox equations:

a) $NH_3 + O_2 \longrightarrow NO + H_2O$ (2, 5/2 ⟶ 2,3)*

b) $C_6H_{14} + O_2 \longrightarrow CO_2 + H_2O$ (1, 19/2 ⟶ 6,7)

c) $Zn + AgNO_3 \longrightarrow Zn(NO_3)_2 + Ag$ (1, 2 ⟶ 1,2)

* It is correct to balance an equation using coefficients containing fractions. Remember that these coefficients represent the number of moles and one could certainly measure out ½ mole of a compound.

SECTION 2: STOICHIOMETRY

A balanced chemical equation not only reveals the symbols and formulas of substances reacting and producing products but shows the precise molar relationship among the substances. The equation in the first worked example of section 1 can be translate to read: "one mole" of propane reacts with "five moles" of oxygen to produce "three moles" of carbon dioxide and "four moles" of water. Computations based on formula and balanced equations are referred to as stoichiometric calculations. This unusual word is derived from the Greek "stoicheion" meaning element and "metria" for science of measuring. Stoichiometry is the mathematical relationship between the numbers of moles of one reactant or product to the number of moles of another reactant or product. It can be determined simply by examining the balanced equation.

For a generalized equation:

$$aA + bB \longrightarrow cC + dD$$

where A and B are reactants
C and D are products
a,b,c, and d represent the appropriate coefficients

the stoichiometric relationsnip between the number of moles of one reactant or product to the number of moles of another reactant or product can be determined by finding the ratios of the appropriate coefficients.

For example:

$$\text{number of moles D} = \frac{d}{a} \text{ times number of moles A}$$

In order to balance an equation the products must be given or be predictable. A few general chemistry equation types should be memorized to assist in product predictions and equation balancing.

a) Acids + Base $\longrightarrow$ Salt + Water

b) Nonmetal Oxides + Water $\longrightarrow$ Acids

c) Metal Oxides + Water $\longrightarrow$ Hydroxides

d) Metals (active) + Acid $\longrightarrow$ Hydrogen + Salts

e) Hydrocarbons + Oxygen $\xrightarrow{\Delta}$ Carbon Dioxide + Water

where: Δ indicates ignition or heat source.

Student Problems

1. Given the following equation, calculate the number of moles of oxygen required to form 25 moles of ZnO. (12.5 moles O_2)

$$2\ Zn + O_2 \longrightarrow 2\ ZnO$$

2. How many moles of $MgCl_2$ will be produced from 6 moles of HCl and an excess of $Mg(OH)_2$? (3 moles $MgCl_2$)

3. Predict the actual products from the following reactants by selecting the appropriate "general chemistry equation" type.

a) $SO_3 + H_2O \longrightarrow ?$ (H_2SO_4)

b) $Al + HNO_3 \longrightarrow ?$ $(H_2,\ Al(NO_3)_3)$

c) $C_6H_6 + O_2 \longrightarrow ?$ $(CO_2,\ H_2O)$

SECTION 3: THEORETICAL AND ACTUAL YIELDS

You should recall that a mole or gram molecular weight of a substance is the number of grams corresponding to the substance's total atomic or molecular weight. It should be a relatively simple matter to calculate the quantity of any one reactant or product by using the stoichiometric relationship and the known gram molecular weight:

$$\text{number of moles A} = \frac{\text{number of grams A}}{\text{Gram molecular weight A}}$$

The expected (theoretical) quantity of product calculated in this way from a given quantity of reactant is called the theoretical yield of the product.

Worked Example

When 116.0 g of butane (C_4H_{10}) are burned to give CO_2 and H_2O, what is the theoretical yield in both (a) moles and (b) grams of CO_2?

Balanced Equation:

$$C_4H_{10} + 13/2\ O_2 \longrightarrow 5\ H_2O + 4\ CO_2$$

$$\text{number of moles A} = \frac{\text{number of grams A}}{\text{Gram molecular weight A}}$$

$$\text{number of moles } C_4H_{10} = \frac{116.0\ g\ C_4H_{10}}{58.0\ g/GMW}$$

$$\text{number of moles } C_4H_{10} = 2$$

(a) According to the balanced equation, 1 mole C_4H_{10} will give 4 moles of CO_2, therefore 2 moles C_4H_{10} should yield **8 moles CO_2.**

(b) Number of moles D = $\frac{\text{number of grams D}}{\text{Gram molecular weight D}}$

$$8 \text{ moles } CO_2 = \frac{\text{number of grams } CO_2}{44.0 \text{ g/mole}}$$

Number of grams CO_2 = 8 moles CO_2 x 44.0 g/mole

Number of grams CO_2 = **352 g**

Student Problems

1. Calculate the number of grams of water required to react stoichiometrically (quantitatively) with 9.66 g of pure sodium metal according to the following equation. (7.56 g H_2O)

$$2 \text{ Na} + 2 \text{ } H_2O \longrightarrow H_2 + 2 \text{ NaOH}$$

In practice, the actual yield of products from a reaction is never as great as the theoretical yield. The actual yield is always less than the theoretical yield. The actual percentage yield is calculated using the following formula:

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

where actual and theoretical yield may be expressed in any convenient units (grams, pounds, moles, etc.), but both yields must be measured by the same units.

Worked Example

1. The actual yield of H_2O collected when 20.0 g of hydrogen gas (H_2) was burned in excess oxygen was 160 g. What was the percentage yield of H_2O in this experiment?

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$$

Theoretical

$$\text{number of moles } H_2 = \frac{\text{number of grams } H_2}{\text{gram molecular weight } H_2}$$

$$= \frac{20.0 \text{ g}}{2.0 \text{ g/moles}} = 10 \text{ moles}$$

According to the balanced equation, 1 mole H_2 yields 1 mole H_2O therefore 10 moles H_2 should yield 10 moles H_2O.

$$\text{number of moles } H_2O = \frac{\text{number of grams } H_2O}{\text{gram molecular weight}}$$

$$10 \text{ moles } H_2O = \frac{\text{number of grams } H_2O}{18.0 \text{ g/moles } H_2O}$$

$$\text{number of grams } H_2O = 10 \text{ moles} \times 18 \text{ g/moles}$$

$$= 180 \text{ g}$$

Theoretical Yield = 180 g
Actual Yield = 160 g

$$\% \text{ yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

$$\% \text{ yield} = \frac{160 \text{ g}}{180 \text{ g}} \times 100 = \boxed{89\%}$$

Student Problem

1. Calculate the % yield of oxygen (O_2) if the actual yield of oxygen from heating 16.93 g BaO_2 is 0.800 g. (50%)

$$BaO_2 \longrightarrow BaO + \frac{1}{2} O_2$$

SECTION 4: LIMITING REAGENT

Chemical equations specify exactly how much of one reactant is required to "consume" a given amount of any other reactant. If one reactant is present in excess, the excess quantity will not be consumed. The reactant present in the smallest quantity relative to that specified by the chemical equation is called the limiting reagent inasmuch as it limits the theoretical yield.

Worked Example

If 5 moles of CH_4 are burned in 5 moles of O_2 according to the following equation, which compound is the limiting reagent?

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$$

It is obvious from the balanced equation that 2 moles of oxygen are "consumed" for each mole of CH_4 available. Thus 5 moles of CH_4 would require 10 moles of O_2. Oxygen is the limiting reactant.

Laboratory

A gravimetric determination (analysis by measuring weights) demonstrates the principle of quantitative analysis at this point.

Determining the iron content in an ore sample would illustrate this technique. A generalized step-wise procedure for any gravimetric determination is as follows:

1. Dissolve a known weight of the sample containing the ion of interest.
2. Add to the solution a substance that will form an "insoluble" compound with the ion of interest. The solubility of this compound must be so small that the weight of the ion remaining in solution is too low to be measured with the laboratory instruments available.
3. Collect the compound by filtration.
4. Wash the compound to remove soluble contaminants.
5. Dry the compound and weigh it. If the compound has been collected in filter paper, the paper must be burned off so that only the pure, dry compound remains.
6. Calculate the weight of the ion of interest contained in the precipitate.
7. Calculate the percentage by weight of the ion of interest in the original sample.

Student Problems

1. What is the limiting reactant when 10.0 g of methane are burned in 25 g of oxygen? (Oxygen)
2. Sodium reacts with chlorine to give sodium chloride. If 50.0 g of sodium metal is mixed with 75.0 g of chlorine (Cl_2) which is the limiting reagent? (Cl_2, since 50.0 g of sodium requires 77.1 g of Cl_2 to react completely.)

3. 45.0 grams of zinc and 28.0 grams of sulfur are intimately mixed and caused to react until one is completely consumed. How many grams of zinc sulfide will be formed? How many grams of which element will remain unreacted? (5.98g S remains)

4. The reaction of a dry cell may be represented by $Zn + 2\ NH_4Cl \longrightarrow ZnCl_2 + 2\ NH_3 + H_2$. Calculate the number of grams of zinc consumed during the release of 9.32 grams of ammonia in such a cell. (17.9 g)

5. The explosion of nitroglycerine is described by the equation $4\ C_3H_5(NO_3)_3 \longrightarrow 12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2$. How many grams of carbon dicxide are produced by the explosion of 69.7 grams of nitroglycerine? (38.5 g)

6. A solution containing 1.46 grams of barium chloride is added to a solution containing 2.14 grams of sodium chromate, Na_2CrO_4. Find the number of grams of barium chromate that precipitate. (1.78g $BaCrO_4$).

Chapter III

Electrochemistry

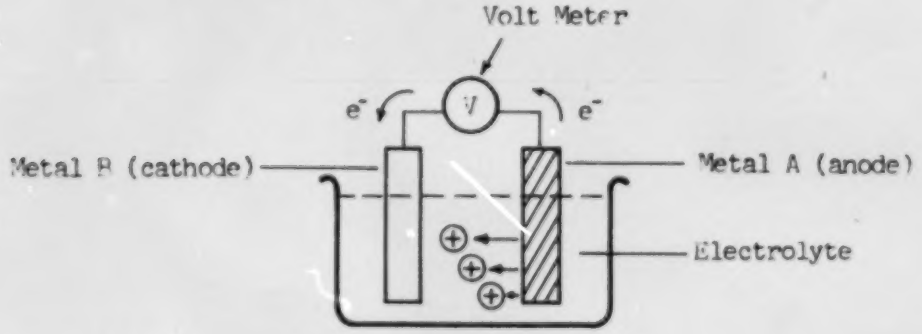
SECTION 1: THE GALVANIC CELL

Whenever two unlike metals are electrically connected together a voltage is produced between them. If two metals are placed into a conducting solution, the electrical potential can cause metal ions to leave the more positive metal, the anode, and to move to the more negative metal, the cathode. The anode and cathode are called electrodes. Any conducting solution is called an electrolyte. The conduction in an electrolyte is caused by the migration of ions through a potential difference. An arrangement of materials which result in a chemical reaction that generates an electric current is called a galvanic or voltaic cell. The chemical reaction in a galvanic cell is an oxidation-reduction reaction. In the cell illustrated below, metal "A" is oxidized at the surface of the anode; the metal "A" ions are reduced at the cathode. When ions are reduced, they may coat metal "B" with a layer of "A". The cathode will then grow larger while the anode is growing smaller.

$$A \longrightarrow A^+ + e^- \quad \text{anode reaction (oxidation)}$$

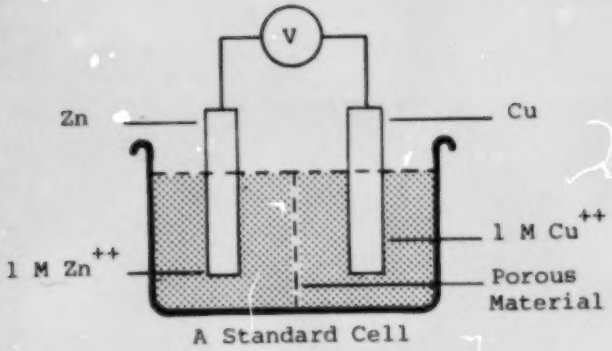
$$A^+ + e^- \longrightarrow A \quad \text{cathode reaction (reduction)}$$

The cathode reaction is not limited to A^+ ions; any positive ion will migrate towards the cathode. Positive ions are called cations. Negative ions are called anions; they migrate towards the anode.



GALVANIC CELL

The voltage produced by a galvanic cell depends upon the two metals and the concentration of ions in the electrolyte. A standardized measurement of the voltage that a metal will create is done with a Standard Cell. A standard cell is composed of two standard half-cells. These half-cells consist of a pure metal electrode in an electrolyte whose concentration is 1M in ions of that metal. The half cells are connected by a porous material or a salt bridge which allows ion migration yet keeps the solutions from mixing. Such cells are used principally for measurement of potential differences (without current flowing).

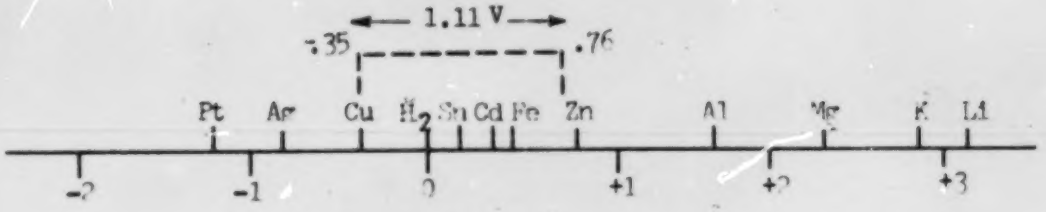


A Standard Cell

The potential created by standard cells can be used to rate the metals in terms of their tendency to oxidize. Thus, tables of Standard Oxidation Potentials can be created. On this table the oxidation potential of hydrogen is made zero since potentials are measured as potential differences and require a reference (i.e. ground potential). The table is a partial list. Any oxidation-reduction reaction has a standard oxidation potential.

TABLE OF STANDARD
OXIDATION POTENTIALS

Half Reaction	Potential (volts)
$Li \rightleftharpoons Li^{+} + e^{-}$	+3.06 volts
$K \rightleftharpoons K^{+} + e^{-}$	+2.92
$Mg \rightleftharpoons Mg^{2+} + 2e^{-}$	+2.34
$Al \rightleftharpoons Al^{3+} + 3e^{-}$	+1.67
$Zn \rightleftharpoons Zn^{2+} + 2e^{-}$	+ .76
$Fe \rightleftharpoons Fe^{2+} + 2e^{-}$	+ .44
$Cd \rightleftharpoons Cd^{2+} + 2e^{-}$	+ .40
$Sn \rightleftharpoons Sn^{2+} + 2e^{-}$	+ .14
$H_2 \rightleftharpoons 2H^{+} + 2e^{-}$	0.0
$Cu \rightleftharpoons Cu^{2+} + 2e^{-}$	- .35
$Ag \rightleftharpoons Ag^{+} + e^{-}$	- .80
$Pt \rightleftharpoons Pt^{2+} + 2e^{-}$	-1.20



Standard
Oxidation Potentials (Volts)

The potential difference measured between two standard half-cells is the difference between the two standard potentials. For example 1.11 V would be measured between a standard Zn half-cell and a standard Cu half-cell. The zinc would be oxidized because it has a higher oxidation potential than does copper. The zinc would become the anode.

Student Problem

1. Fill in the following table describing various combinations of standard half-cells.

Metal A	Metal B	Potential Created	Metal Oxidized	Cathode Metal	Anode Metal
Sn	Cu				
Pt	Cu				
Zn	Mg				
Li	H_2				

Whenever the concentration in a cell is not 1M as it is in standard cells, the potential created is different. Concentrations seldom are 1M in actual practice. For concentrations other than 1M, the Nernst Equation is used to calculate the potential. For reactions of the type

$$M \longrightarrow M^{n+} + ne^-$$

the Nernst equation can be written

$$E = E^o - \frac{.059}{n} \log [M^{n+}]$$

where

E^o is the standard oxidation potential
n is the oxidation number change
$[M^{n+}]$ is the ionic molar concentration
E is the cell oxidation potential

Worked Example

1. What would be the potential difference between a half-cell made of zinc in .001 M Zn^{2+} and a half-cell made of copper in a .1 M solution of Cu^{2+} ions where: $Zn(s) + Cu^{2+} \longrightarrow Zn^{2+} + Cu(s)$

   The potential created by the zinc half cell

   $$E = .76 - \frac{.059}{2} \log .001$$

   $$= .76 - (.03)(-3) = .76 + .09 = +.85 \text{ volts}$$

   The potential created by the copper half cell

   $$E = -.35 - \frac{.059}{2} \log .1$$

   $$= -.35 - (.03)(-1) = -.35 + .03 = -.32 \text{ volts}$$

   The difference between these two is the answer

   $$.85 - (-.32) = 1.17 \text{ volts}$$

Student Problem

1. Use the Nernst Equation to determine the potential differences obtained between the following pairs of half cells.

   (1) Zinc in .01 M Zn^{2+} and copper in .001 M Cu^{2+}. (1.08 V)

   (2) Silver in 10 M Ag^{2+} and cadmium in 1 M Cd^{2+}. (1.23 V)

   (3) Copper in 10 M Cu^{2+} and copper in .001 M Cu^{2+}.

The answer to (3) above is 0.12 V. This is an example of a concentration cell in which the metal is the same, but a potential difference is caused by a difference in electrolyte concentration.

SECTION 2: THE CORROSION OF IRON AND STEEL

Steel usually rusts by an electrochemical process called oxygen absorption. All that is required is oxygen in the air and an electrolyte, which can simply be moisture in the air. An electrochemical cell is formed between an anode, (iron) and a cathode (another part of the surface) in contact with an electrolyte. The reaction is due to a potential difference within the metal between the anode and the cathode. The presence of salt in the electrolyte will accelerate the corrosion process. Salt, such as that used for ice removal on winter streets or as in ocean breezes, makes the electrolyte more conductive.

Iron and steel want to rust. These metals began as iron oxide ores, found in nature. Great amounts of energy and time were required to separate the iron from the oxygen.

Student Problems

1. Write and balance the full chemical equation of the rusting in iron. Assume the final end product is Fe_2O_3.

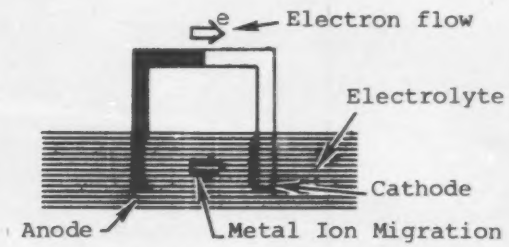
2. List three requirements for the rusting of steel and suggest three means to prevent rust by eliminating the possibility of fulfilling the requirement.

SECTION 3: GALVANIC CORROSION

The corrosion of any metal involves an oxidation-reduction process in which the metal is oxidized to a compound. All oxidation-reduction processes are associated with an electrical potential difference which specifies the cathode and the anode. Metal is removed from the anode as it is oxidized. The specific locations of the cathode and anode are often determined by design, environment or the internal metallurgical variations. Potential differences can be caused in fabricated materials by several mechanisms:

1) compositional variations
2) concentration variations
3) temperature
4) localized stress
5) crystal size

Each of these can produce the potential difference required to cause corrosion of a metal structure. Compositional variations between two metals in direct contact produce an anode and a cathode. This can result in galvanic corrosion and is common in assemblies of dissimilar metals. Metals are commonly listed in order of electrochemical "force," a list called the galvanic series. Metals higher on the list become an anode and corrode when paired with metals lower on the list.



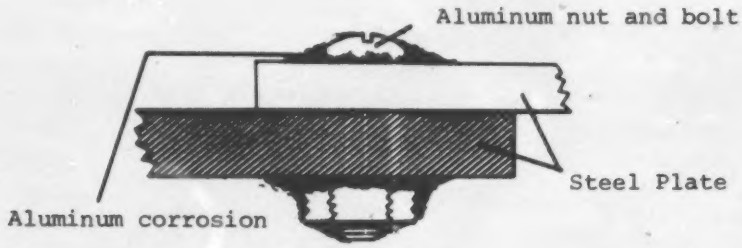
Galvanic Series of Metals

Corroded End (anodic, or least noble)

Magnesium
Zinc
Aluminum 1100
Cadmium
Steel
Cast iron
18-8 Stainless
Tin
Nickel
Brasses
Copper
Bronzes
Titanium
Silver
Graphite
Gold
Platinum

Protected End (cathodic or more noble)

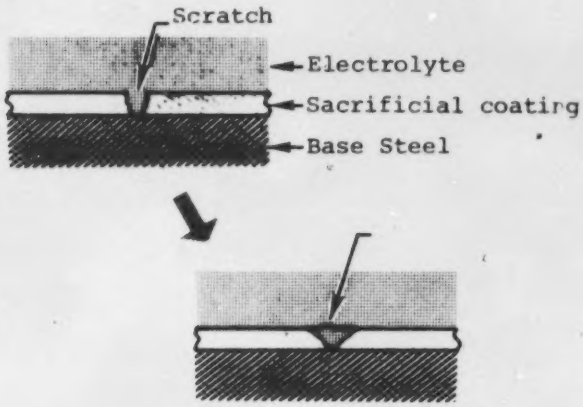
An example of how galvanic corrosion works is observed when an aluminum nut and bolt is used to connect steel plate. In a moist or seaside atmosphere the aluminum will corrode easily. Note that aluminum is above steel in the galvanic series.



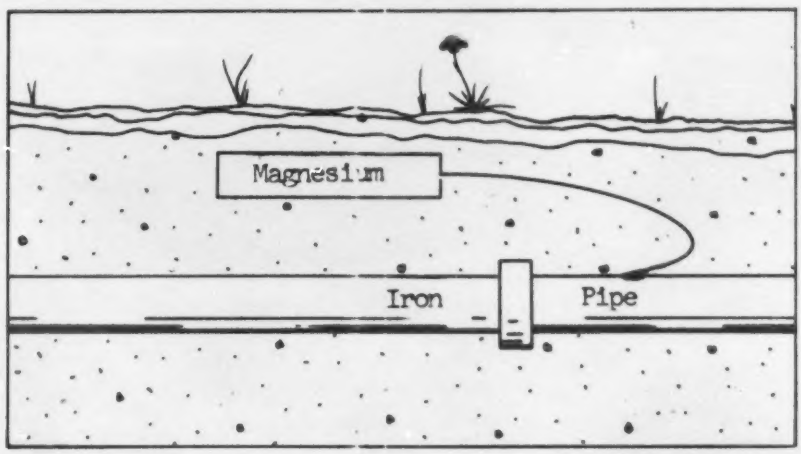
If an aluminum self-threading screw is used on zinc plate, the opposite will occur. Zinc is above aluminum in the galvanic series, thus zinc will corrode.

In designs where contact between dissimilar metals is unavoidable, it is best to provide the anodic part with as large a surface as possible to distribute the corrosive damage. For example, at a Zn-Al junction, illustrated above, damage to the anodic zinc is spread over the large surface of the zinc plate. On the other hand, at the Al-steel junction, severe damage is concentrated on the small surface area of the anodic nut and bolt.

The galvanic effect is used to protect steel from rusting. A coating made from a metal higher on the galvanic series can be made into a sacrificial coating. Zinc is most commonly used. The process is known as galvanization. If a zinc galvanized steel is scratched or nicked to expose bare steel, the anodic coating sacrificially deposits over the steel, preventing rust. Cadmium coatings are also used to protect steel in this way. A tin coating over steel will not protect against rust once the tin has been scratched. Tin is below steel in the galvanic series thus the iron becomes the anode and will freely rust. Tin plating is used as protection of steel because it blocks the attack of oxygen and water. Once the tin is scratched, corrosion begins.



Galvanization is a form of cathodic protection. Cathodic protection is a technique used to prevent or retard the corrosion of one metal. For example, an iron or steel underground pipe can be connected by a wire to a more active metal such as zinc, aluminum, or magnesium. The difference in activity of the two metals causes a current to flow between them, producing corrosion of the more active metal. The active metal supply can be replaced periodically leaving the underground pipe intact.



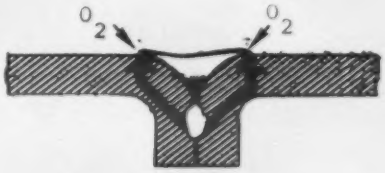
Cathodic Protection

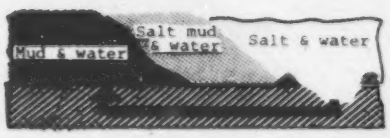
Many ocean-going ships and boats have large pieces of sacrificial zinc placed near brass propellors and shafts. This is a form of cathodic protection. The zinc need not be connected directly to the brass since the salt water is a good conductor. The zinc, being above brass in the galvanic series, corrodes rather than the brass. The process known as dezincification is galvanic corrosion on a microscopic scale. Microscopically, many alloys consist of two or more phases. These can form small galvanic corrosion cells. For example, brass can consist of small interlaced copper-rich and zinc-rich phases. The zinc becomes the anode and, in the presence of an electrolyte, it will corrode, leaving behind a very porous copper-rich phase which has little strength.

Several examples of galvanic corrosion are shown in the following examples with the heavy arrows indicating the direction of electron flow.

A potential difference is established between an oxygen-starved surface and a surface where oxygen is plentiful. Rusting, for example, begins at the node formed in the center of a droplet or a stagnant puddle of water where oxygen is scarce. Cathodic reaction takes place at the outer edges where oxygen is available. The large arrows show the direction of electron flow.

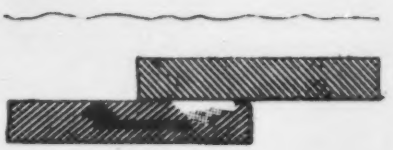
Crevice corrosion is caused by an oxygen gradient between the electrolyte at the surface and the oxygen-starved electrolyte at the bottom of the crevice. This condition is typical of weldments, sheet-metal joints, and rough surfaces where water may be trapped, and also explains why a rough microfinished surface rusts faster than a smooth surface.





Gradients in electrolyte composition are probably the most common cause of rust. Pipes in soil, for example, passing through strata with varying salt content, and car fenders collecting clumps of mud with salt and water of varying concentration are conditions that encourage very rapid rusting.

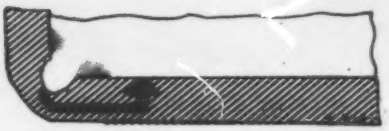
A less obvious form of crevice corrosion takes place between tightly sealed joints where the concealed metal surface is oxygen starved. Electrolyte may seep between irregularities in the mating surfaces or may be carried by moisture-bearing materials (such as wood) in contact with the steel.



A galvanic cell can even be created within a piece of metal which has a uniform concentration. They are caused by changes in crystal structure brought about by localized stresses and by residual stresses created when metal is bent or deformed.

Steel can also rust all by itself--due to internal metallurgical differences. The microscopic grains in a piece of steel are comprised of a number of crystalline structures and a potential difference can exist between them. Even variations in grain structure or heat treatment within a metal can set up potentials that drive rusting reactions.

Localized stresses in steel change electrical potential. Generally, a point of applied stress becomes an anode. The phenomenon is especially critical in structural parts because the metal degenerates where strength is most needed.



Even localized residual stresses provide anode points: formed or bent steel parts bearing residual stresses near the point of deformation, surface-hardened or conversion-coated parts with compressive residual stresses at the surface, and even welded metal that may be stressed near the weld zones, for example. This phenomenon explains why sheet steel often rusts first at bent edges.

Student Problems

1. If a tin plate is contacted to a cadmium plate, will a galvanic cell be created in a moist atmosphere? If corrosion were to occur, which metal would be oxidized? Which metal would be corroded? (Yes, cadmium, zinc)

2. Which is best to use: 1) a steel bolt in a large brass plate, or 2) a brass bolt in a large steel plate? (Brass bolt)

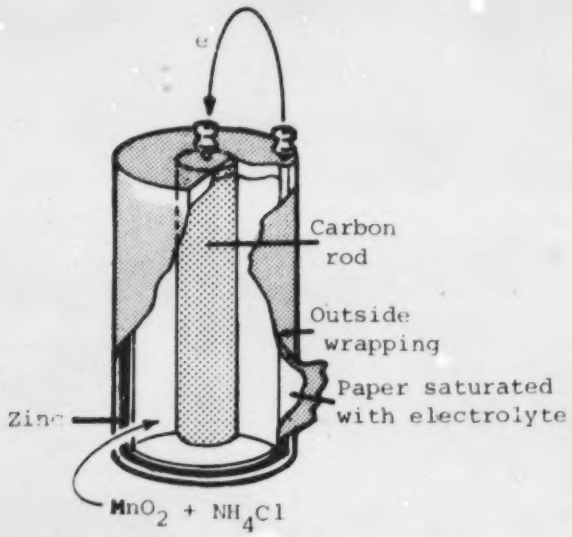
3. Large blocks of magnesium are often dropped at the base of off-shore oil drilling rigs. Why is this done? (Cathodic protection)

SECTION 4: APPLIED ELECTROCHEMISTRY

Voltaic cells are galvanic cells in which a chemical reaction creates an electric potential. The common dry cell is an example of a voltaic cell. The chemical reaction involves two half-cell reactions:

(oxidation) half cell: $Zn \longrightarrow Zn^{2+} + 2e^-$

(reduction) half cell: $2MnO_2 + 2NH_4^+ + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$



A potential of approximately 1.5 volts is generated between the positive carbon electrode and the negative zinc can.

The lead storage battery is another common example of a voltaic cell. The automobile battery is constructed of alternating plates of lead and lead dioxide immersed in sulfuric acid (electrolyte). When the battery is in use, the lead plate (Pb^0) is the positive pole (anode) and the lead dioxide (PbO_2) is the negative pole (cathode). The following half-reactions take place simultaneously:

Anode: $Pb \longrightarrow Pb^{2+} + 2e^-$

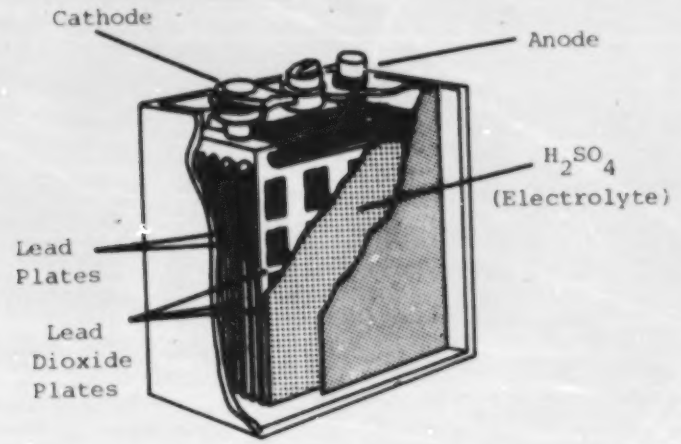
then: $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

Cathode: $PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O$

then: $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

It should be noted that as this type battery discharges, H_2SO_4 (specific gravity: 1.28) is consumed and water is being produced. Thus, a simple check of the specific gravity could indicate the state of "charge". A completely discharged battery will have a specific gravity very close to that of water (1.08).



Lead Storage Battery

The lead storage battery unlike most other common voltaic cells can be recharged. An electrolytic cell is a cell in which a chemical reaction is forced to occur by the application of an outside source of electricity (an alternator for example).

$$2PbSO_4 + 2H_2O \underset{\text{discharge}}{\overset{\text{recharge}}{\rightleftharpoons}} Pb + PbO_2 + 2H_2SO_4$$

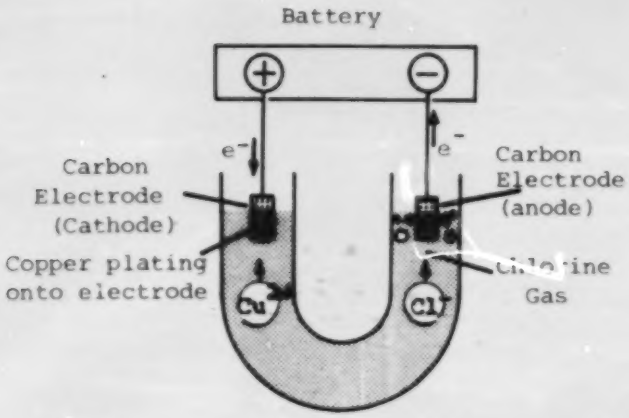
A fuel cell is a special example of both a voltaic and electrolytic cell. Using the chemical energy of a fuel and an oxidizing agent, electrical energy is produced directly. A fuel cell can be created using any two or more elements, for example with hydrogen (fuel) and oxygen (oxidizing agent).

$$2H_2 + O_2 \longrightarrow 2H_2O + \text{electrical energy}$$

By reversing the above reaction, both gaseous hydrogen and oxygen can be generated from water by applying an electric current. This process is called electrolysis.

$$2H_2O + \underset{\text{energy}}{\text{electrical}} \longrightarrow 2H_2\uparrow + O_2\uparrow$$

Another example of electrolysis (the forcing of a chemical reaction by applying an electric current) can be demonstrated by passing a current through a copper chloride solution. The following reaction takes place with copper plating out on the cathode and chlorine gas being liberated at the anode.



Electrolysis of a $CuCl_2$ Solution

Faraday's Law states that the amount of chemical change produced by an electric current is directly proportional to the quantity of electricity used. The quantity of electricity is actually the number of electrons involved. The standard unit of electricity is the coulomb and was originally defined as the quantity of electricity needed to plate 1.118×10^{-3} g of silver from a silver ion solution. An important chemistry application can be derived from Faraday's Law by the fact that "the equivalent weight of a substance is the number of grams that can gain or lose one mole of electrons". (e.g. 6.023×10^{23} electrons)

One Faraday = 96,500 coulombs = 1 mole of electrons = 6.023×10^{23} electrons

thus

One Faraday = the charge carried by 1 GEW

Current flows are normally expressed in amperes. One ampere is equal to the flow of one coulomb per second through a conductor. For example, a 1 ampere current would require 96,500 seconds to deposit one mole of electrons.

$$\boxed{\text{coulombs} = \text{amperes} \times \text{seconds}}$$

Worked Example

1. Calculate the theoretical quantity of copper (Cu) and chlorine gas (Cl_2) produced by the passage of 96,500 coulombs through molten copper (II) chloride.

$$Cu^{2+} + 2e^- \longrightarrow Cu \quad \text{(reduction)}$$

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad \text{(oxidation)}$$

$$\text{gram-equivalent weight copper} = \frac{63.55}{2} = 31.78 \text{ g}$$

$$\text{gram-equivalent weight chlorine} = \frac{35.45}{1} = 35.45 \text{ g}$$

Since: 96,500 coulombs = 1 faraday = charge carried by 1 GEW

then

$$\boxed{Cu = 31.78 \text{ g}}$$

$$\boxed{Cl_2 = 35.45 \text{ g}}$$

2. How many coulombs of charge will be required to plate out 10.2 g of iron from a solution of iron (II) chloride?

$$\text{GEW (iron)} = \frac{55.85}{2} = 27.93$$

thus 27.93 g iron are deposited by 96,500 coulombs = 1 faraday

$$\text{or charge} = 10.2 \text{ g} \times \frac{1 \text{ faraday}}{27.93 \text{ g}} \times \frac{96{,}500 \text{ coulombs}}{1 \text{ faraday}}$$

$$\boxed{\text{charge} = 35{,}240 \text{ C}}$$

3. How much time (seconds) would be required to plate out the 27.93 g of iron in problem 2 using a 20.0 ampere current?

$$\text{coulombs} = \text{amperes} \times \text{seconds}$$

$$\text{seconds} = \frac{\text{coulombs}}{\text{amperes}}$$

$$\text{time} = \frac{35{,}240 \text{ coulombs}}{20.0 \text{ amperes}}$$

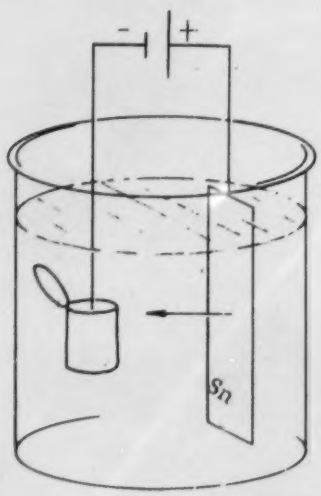
$$\boxed{\text{time} = 1760 \text{ s}}$$

Student Problems

1. Determine the number of hours required for a 6.0 ampere current to electrolytically decompose 18.0 g of water. (9 hours)

2. An electrolytic cell contains a solution of copper (II) sulfate and an anode of impure copper metal. Calculate the quantity of copper that will be deposited on the cathode by 150 amperes maintained for exactly 1 hour. (178 grams)

Electroplating is a process whereby a metal surface is coated with another metal using an electrical current.



Electroplating a steel can with tin

When a metal is electroplated with zinc, it is said to be galvanized. This may seem to be a strange metal to select to protect iron since zinc is higher on the activity scale than iron. Zinc (like iron) reacts readily with moisture, oxygen, and carbon dioxide but forms a tough film of $Zn(OH)_2 \cdot ZnCO_3$ that resists further attack. This is plated on steel for the same purpose.

Electroplating is one of the most important methods for production of metallic coatings. The most common electrodeposited metals are zinc, nickel, chromium, tin and copper. In recent years alloys such as lead-tin, tin-copper, and tin-zinc have been increasingly electroplated.

Laboratory

The student should have experience performing a simple electroplating experiment, including plating techniques and parameters (solute concentrations, current flow rates, impurities, temperature effects, etc.).

SECTION 5: CORROSION CONTROL AND PREVENTION

The prevention and control of corrosion can be accomplished in several ways:

1. Protection by design and fabrication procedures.
2. Modification of the corrosive environment.
3. Application of inhibitors.
4. Purification and alloying of metals.
5. Cathodic protection.
6. Application of protective coatings.

The proper selection of materials and sound design are the best means of controlling and preventing corrosion. The use of dissimilar-metal contacts should always be avoided because galvanic corrosion could result from the presence of an electrolyte. If two metals are to contact, choose ones that are very close in the galvanic series. The anode area should be as large as possible, and the cathode area should be much smaller. If practical, dissimilar metals should be electrically insulated from one another. If the anode area is painted or coated, any breaks in the layer would lead to rapid penetration of the metal at that point. Uniform corrosion of unpainted anode might be less disastrous.

A corrosive environment is necessary for most corrosive processes. Oxygen dissolved in water is a major cause of iron corrosion. Oxygen can be removed by deactivation at high temperature or by chemical deactivation. Sodium sulfite is frequently used; it reacts with oxidizing agents to form soluble sodium sulfate.

Dehumidification is the process of reducing air moisture to such an extent that the amount of water condensed on surfaces is negligible and corrosion is minimal.

A corrosion inhibitor is a substance which effectively decreases the corrosion rate of metal when added in small amounts to the corrosive environment. They can be divided into anodic and cathodic types according to their effect on the respective electrode. Anodic inhibitors stifle corrosion by forming a slightly soluble compound with the newly produced metal ion. The compound coats the anode area and protects it. Cathodic inhibitors modify the cathode reaction in such a way that it can be more easily controlled.

Pure metals have higher corrosion resistance than do impure metals. However, very pure metals are more expensive and do not have the diversified mechanical properties of alloys. Alloys have been developed specifically for corrosion resistance. If aluminum, magnesium or lead are alloyed, they form two-phase heterogeneous alloys having low corrosion resistance. However, metals like iron, nickel, chromium, copper and cobalt form homogeneous solid solutions with many other metals. These alloys can be developed to resist severe corrosive environments. Stainless steel is an example. The chromium in stainless steel produces an oxide surface film which slows down corrosion by oxygen.

Metals such as aluminum, titanium and stainless steel form a persistent protective film on the anode surface in oxidizing environments. Aluminum is very high on the galvanic series yet it withstands weathering well because of its oxide coating. The surface reaction which forms an oxide that inhibits corrosion is called passivation. The commercial process that produces a protective coating on aluminum is called anodizing.

Surface coatings can be used to stop corrosion. Painting is a logical first step. However, a typical film of paint does not adhere well to a smooth metal surface. Also, ordinary paints do not stop the electro-chemical reaction that causes rust. Electrons readily migrate through most paints. Special rust preventative paints such as zinc-rich primers are required.

Before paint is applied to a metal surface for protection, that surface is usually pretreated. Pretreatment can include cleaning and abrading or even chemical conversion. Iron surfaces are often chemically converted to iron phosphate, producing a rough, electrically neutral layer which inhibits electrochemical rusting reactions.

Protection by galvanizing has already been discussed. This is an application of cathodic protection.

Chapter IV

Gas Laws

SECTION 1: GAS PRESSURE

Pressure is defined as the force acting on a unit area of surface. For example, an expression might be:

$$\text{Pressure (in dynes/cm}^2\text{)} = \frac{\text{Force (in dynes)}}{\text{Area (in square centimeters)}}$$

The recommended International System of Units (SI) pressure unit is the pascal. The pascal (Pa) is based on the newton unit of force.

$$\text{Pressure (in pascals)} = \frac{\text{Force (in newtons)}}{\text{Area (in square meters)}}$$

The English system might express:

$$\text{Pressure (in lb/in}^2\text{)} = \frac{\text{Force (in pounds)}}{\text{Area (in square inches)}}$$

Pressure is often expressed in "atmospheres". Since air has weight, it exerts a pressure on the earth's surface. An atmosphere is the pressure exerted by the weight of a column of mercury 760 mm high at $0^{\circ}C$ and is approximately equal to the average pressure exerted by the atmosphere at sea level. The term torr is designed to be used in place of mm of mercury since confusion can arise from the use of a unit of length (mm) as a unit of pressure. One torr is the pressure equivalent to that pressure exerted by 1 mm of mercury.

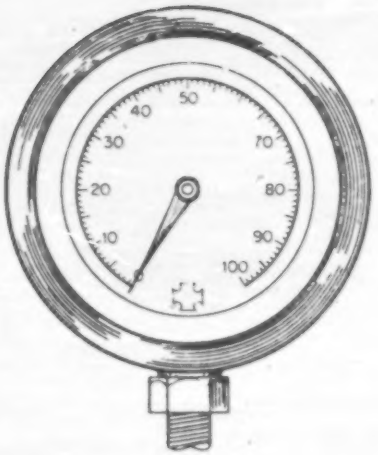
Although atmospheric pressure is recorded on a barometer, the pressure of a confined gas or the vapors of a liquid are normally measured by means of an appropriate gauge. Since atmospheric pressure is being constantly applied to all equipment, pressure gauges usually measure the amount of pressure in excess of atmospheric pressure. The units of a gauge pressure are listed as psig in the English system. The true pressure, called the absolute pressure, is the sum of the gauge pressure and the atmospheric pressure. Thus, in the English system of units,

$$P(\text{absolute}) = P(\text{gauge}) + 14.7 \text{ (in units of psi)}$$

Absolute pressures are listed in units of psia.

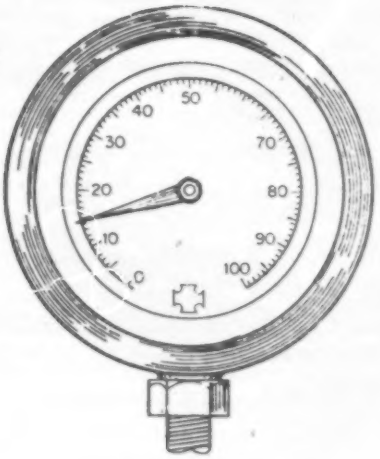
A "psia" gauge indicates the absolute pressure (in the English system) while a "psig" gauge would read 0 psi at one atmosphere. This should be corrected (by adding the barometric pressure) if the absolute pressure is required.

One Atmosphere of Pressure



Gauge Pressure

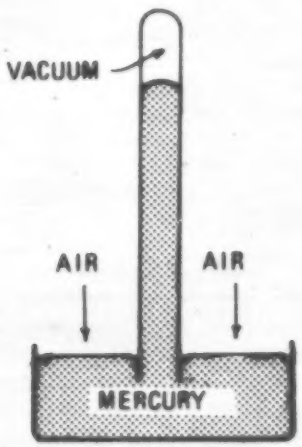
0 psig

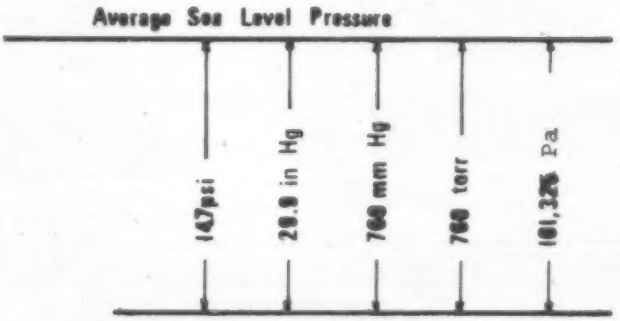


Absolute Pressure

14.7 psia

A barometer is a device used to measure atmospheric pressure. It consists of an evacuated glass tube inverted in a pool of mercury and exposed to atmospheric pressure.





A Torricelli Barometer

Worked Examples

Convert these pressures to "atmosphere" units.

a. 733 mm Hg

$$733 \text{ mm Hg} \times \frac{1 \text{ atmosphere}}{760 \text{ mm Hg}} = 0.965 \text{ atm}$$

b. 435 torr

$$435 \text{ torr} \times \frac{1 \text{ atmosphere}}{760 \text{ torr}} = 0.572 \text{ atm}$$

c. 100,000 Pa

$$100{,}000 \text{ Pa} \times \frac{1 \text{ atmosphere}}{101{,}325 \text{ Pa}} = 0.987 \text{ atm}$$

Laboratory

Each student should review the pressure safety rules given in Chapter 1 of "Chemical Science and Technology I. The student should be able to use a Torricelli type barometer, gas regulators, McLeod and other type pressure gauges, gas drying tubes, etc. The hazards of working with mercury should be discussed.

Student Problems

1. A typical midwest city has a barometric pressure of 740 torr. Express this pressure in both atmospheres and pascals. (0.974 atm; 98,700 Pa)

2. A gas cylinder equipped with a typical "psig" type gauge reads 40 psi. What is the absolute pressure in the cylinder? (54.7 psi)

3. The gauge on a tank registers 74.0 psi. Express this pressure reading in mm Hg. (3830 mm Hg)

SECTION 2: THE IDEAL GAS LAW

At high temperature and low pressures, all gases have been found to obey several simple laws (Boyle's, Charles', Gay-Lussac's, etc.). A gas which obeys these laws is called an ideal gas.

Boyle's Law states that the volume of a gas varies inversely with the pressure, when the temperature is held constant.

$$\text{Volume} \propto \frac{1}{\text{Pressure}} \quad \text{only at constant temperature}$$

Worked Examples

A gas which occupies 200 ml at 25°C has its pressure increased from 1 atm to 6 atm while the temperature is kept constant. What will be the new volume of the gas?

$V_1P_1 = V_2P_2$ where: V_1 and P_1 = Initial volume and pressure

and V_2 and P_2 = Final volume and pressure

$$V_2 = \frac{V_1P_1}{P_2}$$

$$V_2 = \frac{200 \text{ ml} \times 1 \text{ atm}}{6 \text{ atm}}$$

$$V_2 = 33.3 \text{ ml}$$

Charles's Law states that at constant pressure the volume of a given mass of gas varies directly with the absolute temperature.

Volume $\propto$ Temperature (in K)	only at constant pressure

The absolute temperature can be calculated by simply adding 273.15° to the celsius (°C) temperature reading.

Worked Example

A sample of methane gas occupies 3.00 liters at 273 K and 1 atm pressure. If the temperature is raised to 357 K while the pressure remains constant, what will be the new volume?

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

where: V_1 and T_1 = Initial volume and temperature

V_2 and T_2 = Final volume and temperature

$$V_2 = \frac{V_1 \times T_2}{T_1}$$

$$V_2 = \frac{3.00 \text{ liters} \times 357 \text{ K}}{273 \text{ K}} = 3.92 \text{ liters}$$

Avogadro's Law states that equal volumes of different gases under the same condition of temperature and pressure contain the same number of moles. It has been determined that "one mole of any ideal gas will occupy 22.4 liters at standard temperature and pressure". Standard temperature and pressure (STP) means a temperature of 0°C (273 K) and one atmosphere of pressure (760 torr).

Volume $\propto$ moles (n)

Worked Example

How many moles of an ideal gas occupy a volume of 100 liters at STP?

Since 1 mole occupies 22.4 ℓ at STP,

x moles occupy 100 ℓ

where $x = 100\ \ell \left(\frac{1\ \text{mole}}{22.4\ \ell}\right) = 4.46$ moles

The Ideal Gas Law can now be derived by combining Boyle's, Charles's and Avogadro's Laws:

Boyle's Law $V \propto \frac{1}{P}$

Charles's Law $V \propto T$

Avogadro's Law $V \propto n$

$$V \propto \frac{nT}{P}$$

or

$$V = \frac{RnT}{P}$$

$$\boxed{PV = nRT}$$

where: R, the proportionality constant, is the gas law constant which depends on units used to measure P, V and T. See the table below.

Note: The gas law constant (R) is necessary to remove the proportionality sign ($\propto$) in the relationship.

Values and Units of the Ideal Gas Constant "R"
62.4 liter-torr/mole-K
6.24×10^{4} ml-torr/mole-K
0.0821 liter-atm/mole-K
2.90×10^{-3} ft^3 - atm/mole-K
1.99 calories/mole-K
8.37 joules/mole-K

Worked Examples

1. What volume would 3.00 moles of helium occupy at 10° C and 5.00 atmospheres?

$$V = \frac{nRT}{P}$$

$$V = \frac{(0.0821 \text{ liter-atm/mole- K})(3.00 \text{ moles})(283 \text{ K})}{5.00 \text{ atm}}$$

$$V = 13.9 \text{ liters}$$

Note: The gas law constant "R" is selected that will match the other units in the equation and leave the desired unit of expression.

2. At what pressure would 2 moles of nitrogen at 27° C occupy 500 ml? Express the answer in torr.

$$PV = nRT \text{ or } P = \frac{nRT}{V}$$

$$P = \frac{(2 \text{ moles})(6.23 \times 10^4 \text{ torr-ml/mole- K})(300 \text{ K})}{500 \text{ ml}}$$

$$P = 74{,}900 \text{ torr}$$

3. What will be the new volume of 8.00 liters of neon if the pressure and temperature are increased from 2.00 atm and 273 K to 6.00 atm and 400 K, respectively?

$$P_1V_1 = nRT_1 \quad \text{or} \quad nR = \frac{P_1V_1}{T_1}$$

and

$$P_2V_2 = nRT_2 \quad \text{or} \quad nR = \frac{P_2V_2}{T_2}$$

thus

$$V_2 = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times V_1$$

$$V_2 = \frac{2.00 \text{ atm}}{6.00 \text{ atm}} \times \frac{400 \text{ K}}{273 \text{ K}} \times 8.00 \text{ liters}$$

$$V_2 = 3.91 \text{ liters}$$

When a liquid is confined to a closed container at a given temperature, a small amount of it evaporates into the space above the liquid until equilibrium arises between the liquid and its vapor. Equilibrium is characterized by two opposing changes which occur simultaneously. Some of the confined liquid evaporates while vapors of the liquid condense back into the liquid phase. The pressure exerted by the vapor that is in equilibrium with the liquid, at a given temperature, is called the vapor pressure of the liquid at that temperature.

Vapor pressure is a characteristic property of liquids and varies with their temperature. As the temperature of the liquid increases, more and more of the liquid enters the vapor phase. Its associated pressure accordingly increases. When the temperature of a liquid is such that its vapor pressure is equal to the atmospheric pressure, the liquid boils.

VAPOR PRESSURES OF SOME COMMON LIQUIDS

Temperature (°C)	Water (torr)	Ethyl Alcohol (torr)	Mercury (torr)
-10	2.1	5.6	60×10^{-6}
0	4.6	12.2	.000185
10	9.2	23.6	.000490
20	17.5	43.9	.001201
30	31.8	78.8	.002777
50	92.5	222.2	.01267
100	760.0	1,693.3	.2729

Dalton's Law states that the total pressure exerted by a mixture of gases is the sum of the individual partial pressures.

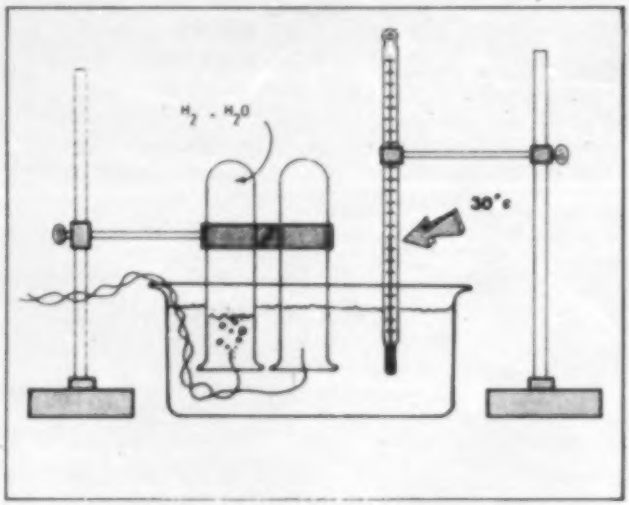
$$\text{Total Pressure} = P_a + P_b + P_c + \ldots$$

where: P_a, P_b, P_c are partial pressures.

Dalton's Law is used to correct for the pressure of water vapor in a gas collected by displacing water. A gas is produced by a chemical reaction and collected by bubbling it into an inverted bottle filled with water. The gas displaces the water but remains saturated with water vapor, which contributes its pressure to the total pressure.

Worked Example

1. Hydrogen gas is produced and collected in a flask by the displacement of water. Calculate the "dry" pressure of the hydrogen gas if the barometer reads 740 torr and the water temperature is 30° C.



Gas Collection by Water Displacement

$$P_{total} = P_a + P_b + P_c + \ldots$$

$$740 \text{ torr} = P_{H_2} + P_{H_2O}$$

P_{H_2O} = 31.8 torr @ 30°C (see vapor pressure table)

thus: P_{H_2} = 740 torr - 31.8 torr

P_{H_2} = 708 torr

A gas will diffuse (distribute itself uniformly) throughout a cylinder in a short period.

Graham's Law states that the rate of diffusion of a gas is inversely proportional to the square root of its molecular weight.

$$\frac{\text{(Rate) A}}{\text{(Rate) B}} = \frac{\sqrt{\text{mol. wt}_B}}{\sqrt{\text{mol. wt}_A}}$$

Worked Example

Compare the rate of diffusion of hydrogen to oxygen.

$$\frac{(\text{Rate})\ H_2}{(\text{Rate})\ O_2} = \frac{\sqrt{\text{mol. wt } O_2}}{\sqrt{\text{mol. wt } H_2}} = \frac{\sqrt{32}}{\sqrt{2}} = \sqrt{16} = 4$$

Thus, H_2 molecules will diffuse 4 times faster than O_2 molecules.

Laboratory

a. The Ideal Gas Law can be demonstrated by having each student determine the molecular weight of a volatile liquid (gas) using the Dumas or Victor Meyer method.

b. Each student should be able to demonstrate Avogadro's Law by collecting hydrogen gas generated from reacting an active metal (e.g. magnesium) with acid and collecting the gas quantitatively by water displacement.

c. The student should perform an experiment in gas sampling.

Student Problems

1. Five gallons of nitrogen gas at 100° C will occupy what volume at 500° C? (Assume pressure remains constant.) (10.4 gallons)

2. A quantity of helium occupies 350 ml at 50° C and 785 torr. What volume will the gas occupy at STP? (306 ml)

3. If 400 ml of an ideal gas weighs 0.536 g at STP, calculate the number of moles of gas and its molecular weight. (0.0179 moles, 30.0 g/mole)

4. What volume will 2.432 g of SO_2 gas occupy at 18° C and 0.993 atm? (0.914 liter)

5. Uranium's isotope 235 is separated from its isotope 238 by reacting both isotopic forms with fluorine and taking advantage of the different diffusion rates. Calculate the relative rates of diffusion assuming that both isotopes form UF_6. (U_{235} = 1.004 and U_{238} = 1.000)

6. The discovery of oxygen occurred from the decomposition of mercury(II) oxide: $2\ HgO \rightarrow 2\ Hg + O_2$. What volume of oxygen would be produced by the reaction of 28.9 grams of the oxide, the gas being measured at STP? (1.49 ℓ O_2)

7. How many liters of oxygen, measured at STP, are required for the complete combustion of 72.0 grams of heptane, C_7H_{16}, a component of gasoline? If air is 21% oxygen by volume, how many liters of air are necessary for this amount of fuel? (Note: CO_2 and H_2O are the only products.) (178 ℓ O_2, 845 ℓ air)

Chapter V

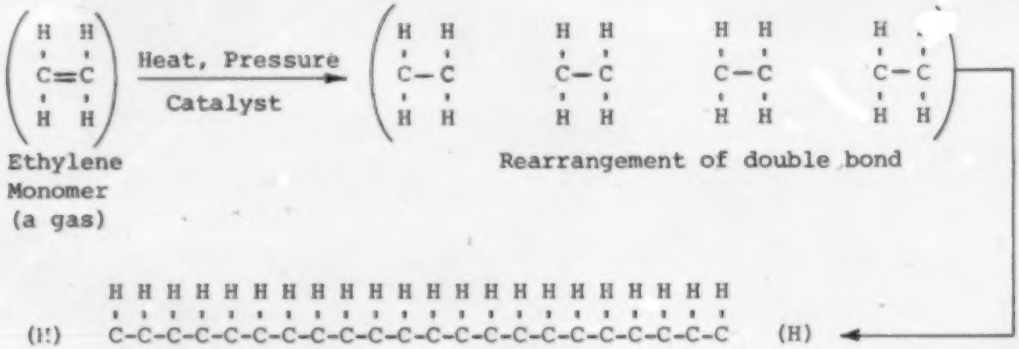
Organic Materials

SECTION 1: CHEMISTRY OF PLASTICS

Students should review the chapter "Organic Chemistry" in the first study guide before starting this chapter on "Organic Materials." The term polymer is used to identify molecules which may have molecular weights as high as a million. (Poly means many; mer means parts.) Polymers are made by joining many small individual molecules known as monomers (mono-means one). A plastic is a synthetic polymer. Plastics can be molded or formed into usable shapes by various processes, usually involving heat and/or pressure. There are over 40 different families of plastics in commercial use today, and each family may have a hundred subtypes.

Plastics are not found in nature. They are synthetically produced by chemically joining many monomers together to form long chains. Often this chemical reaction occurs while the finished article is being formed in a mold. The unreacted chemicals are placed in a mold where they react; the mold is usually heated to speed the reaction. The reaction process is called curing. Plastics which are formed by curing in a mold are called thermosets. There are only two general types of plastics, thermosets and thermoplastics. Thermoplastics are molded or shaped after they have been produced by chemical reactions. The thermoplastics soften or liquify when heated, then harden when cooled in a mold.

The chemical reaction which forms a plastic is called a chain reaction. An example of a chain reaction is the formation of polyethylene. Many familiar articles are made with polyethylene (i.e. laboratory "squeeze bottles"). The monomer is ethylene. When ethylene is subjected to heat and pressure in the presence of a catalyst, the double bonds are broken and the ethylene fragments react to form a chain.



During this reaction, millions of separate polymer chains grow in length simultaneously, until all the monomer is exhausted. The average chain length can be adjusted by the chemist. This chain length determines many of the properties of the plastic. Polyethylene is classified by its average chain length.

Classification of Polyethylene by Chain Length	
Carbons in chain	Polyethylene type
100-1,000	Low molecular weight
1,000-5,000	Medium molecular weight
5,000-50,000	High molecular weight
50,000-500,000	Ultrahigh molecular weight

After the polymerization is completed the polymer chains resemble intertwined bundles of spaghetti, with no connections between chains. Such a polymer is a thermoplastic. Thermoplastics are heat moldable. When this material is molded in a heated mold, there is no significant change in its molecular structure.

Molding of a Thermoplastic Polymer

Many common thermoplastics are formed using common organic monomers. There is a weak electrostatic attraction between chains which lie very close together. This attraction is very heat sensitive, becoming stronger when the plastic is cold. Heating weakens these forces so the chains can slide over each other freely during hot molding. Upon cooling the forces "lock" the molecules together in the new molded shape. Molding thermoplastics is similar to making candles. Too much heat will destroy the molecular chains, and excessive mechanical pressure will cause even a cold thermoplastic object to deform.

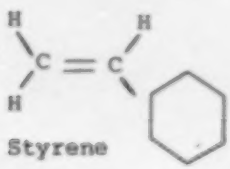
Typical monomers and their repeating polymer units

Monomer	Polymer
Ethylene	Polyethylene
Propylene	Polypropylene
Vinyl Chloride	Polyvinyl Chloride

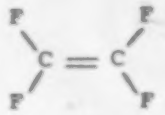
Student Problems

1. Draw a five monomer chain of the plastic, polystyrene. Note that polystyrene will have phenyl branches on the polymer chain.

2. Tetrafluoroethylene is the monomer for polytetrafluoroethylene plastic. Draw a five monomer chain of this plastic.

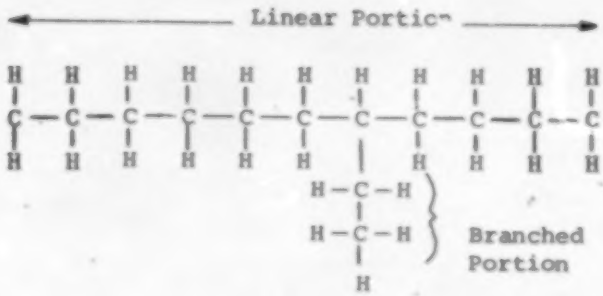


Styrene

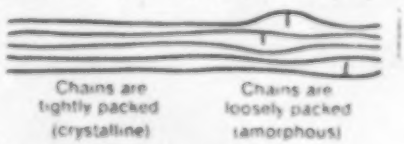


Tetrafluoroethylene

The strength of the intermolecular attraction between chains is very dependent on distance. If polymer chains are symmetrical and packed closely, they will be strongly attracted. The presence of side branches in a chain is common. These can separate adjacent chains and reduce interchain attraction.



If a plastic has few side chains, the strong attraction will create a high density plastic. Another result of this denser packing is higher crystallinity. As symmetrical chains approach a critical distance, crystals begin to form in the areas of densest packing. These crystallized areas are stiffer and have higher tensile strength, while noncrystallized (amorphous) areas are more flexible and have higher impact strength. Crystalline plastics are more difficult to process. They have higher melting temperatures, higher viscosities and they tend to shrink and warp more than the noncrystallized plastics. A plastic material may contain both crystalline and amorphous regions.

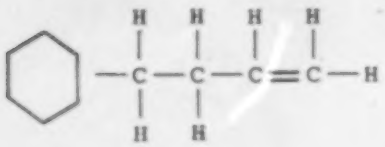


HIGH-DENSITY POLYETHYLENE

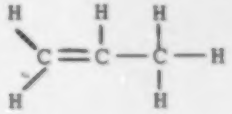
LOW-DENSITY POLYETHYLENE

Student Problem

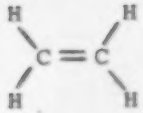
1. Which of the following monomers would be most likely to produce low density polymers? Which would produce the most crystalline polymer?



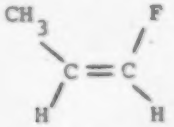
(a)



(b)



(c)

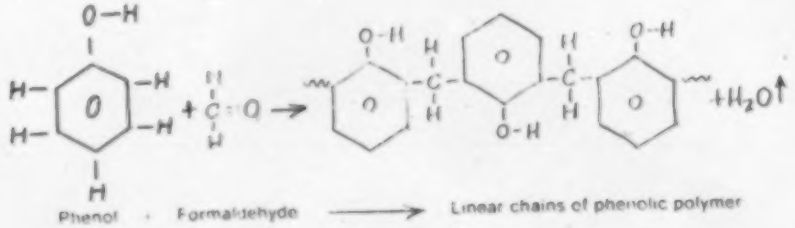


(d)

(c - most crystalline)
(a - low density)

The reactions which form thermoplastics are termed addition polymerization reactions. Addition reactions occur when the reaction takes place between two identical functional groups, the carbon-carbon double bonds. In an addition reaction, only the polymer chain is formed; no other molecule results from the reaction.

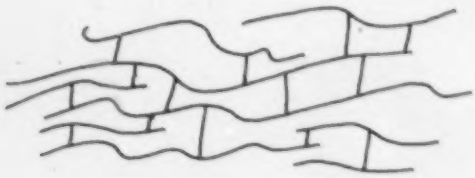
Condensation polymerization reactions occur when reactions between two different functional groups are used for chain growth. These condensation reactions can occur between a carboxyl group and an amide (as with the formation of "Nylon"), between two carbon-carbon aromatic bonds and a carbonyl, or between many other pairs of different functional groups. Condensation reactions create molecules other than the polymer chain, usually water. Thermoplastics are formed only by addition reactions, whereas thermosets are formed by either addition or condensation reactions.



Condensation Polymerization of
Phenolic (Thermoset) Plastic

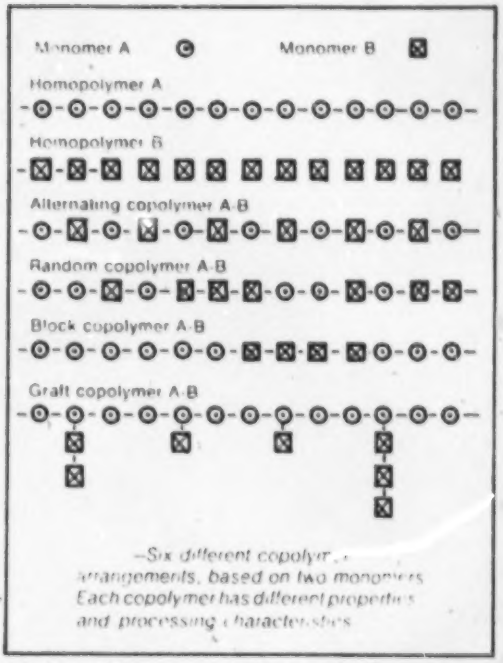
Thermosets derive great structural stability from crosslinking between chains. Crosslinking occurs when polymer chains are linked together by linking groups.

Thermoplastic
with Branching



Thermoset
with Crosslinking

One method of altering molecular symmetry is to use two different monomers (A and B) in the polymerization reaction. Each chain would then contain partly monomer A and partly monomer B. A polymer made of two different monomers is called a copolymer. The final properties of the copolymer will depend on the percentage of monomer A to monomer B and on how they are arranged.

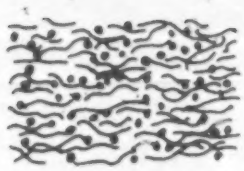


—Six different copolymer arrangements, based on two monomers. Each copolymer has different properties and processing characteristics.

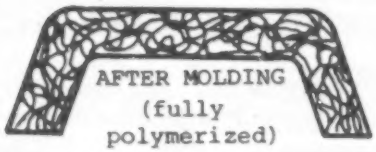
The copolymer can have a repetitive, symmetrical arrangement which would produce a high degree of crystallization. Or the arrangement can be totally random, creating areas of high crystallinity separated by flexible amorphous areas.

Block copolymers have large areas of polymerized monomer A alternating with large areas of polymerized monomer B. These copolymers have great versatility in properties. Graft copolymers are made by attaching side groups of monomer B to a main chain of A polymer.

The curing of thermosets is done in two stages: partly by the materials supplier, and partly by the molder. As illustrated, the thermoset is first partially polymerized by reacting under heat and pressure. The reaction is stopped at the point where mostly linear chains have formed but with little crosslinking. At this point the material is capable of flowing under heat and pressure.



BEFORE MOLDING
(partially polymerized)



Molding of a thermoset polymer

The final stage of polymerization is completed in the molder's press. Here heat and pressure produce the crosslinking. Unlike thermoplastic monomers, which have only two reactive ends for linear chain growth, a thermoset monomer has three or more reactive ends so that molecular chains crosslink in three dimensions. Rigid thermosets have short chains with many crosslinks; flexible thermosets have longer chains with fewer crosslinks.

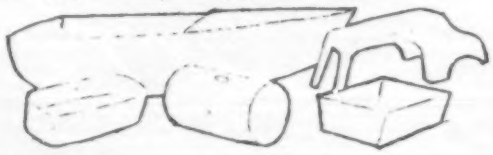
A molded thermoset plastic has virtually all of its polymer molecules interconnected with strong permanent bonds which are not heat reversible. The entire molded part could be one giant molecule. Reheating will not cause remelting, it cannot be remolded. If heated too long, a thermoset will degrade and will never soften for remolding as does a thermoplastic.

Some thermosets are polymerized by condensation reactions (phenolic and melamine for examples). Water is created as the byproduct of the reaction in the mold. This may cause dimensional instability and poor part strength unless the volatile product is carefully removed during the molding.

Other themosets are polymerized by addition reactions (epoxy, polyester, and silicone for example). These reactions have no volatile byproducts.

SECTION 2: SELECTION OF PLASTICS

Plastics selector

General Part Requirement and/or Shape	Typical Candidate Plastics
Structural, Mechanical	
Gears, cams, pistons, rollers, valves, pump impellers, fan blades, rotors	Acetal Nylon Phenolic (reinf) Polycarbonate Polyester (TP) Polyphenylene sulfide
Light-Duty Mechanical and Decorative	
Knobs, handles, battery cases, cable clamps, trim moldings, camera cases, pipe, eyeglass frames, auto steering wheels, handles for hand tools	ABS Acrylic Cellulosics Phenolic Polyethylene Polypropylene Polystyrene PVC
Small Housings and Hollow Shapes	
Telephone and flashlight cases, sports helmets, headlamp bezels; housings for office machines, power tools, pumps, and small appliances	ABS Cellulosics Phenolic Phenylene oxide Polycarbonate Polyester (TP and TS) Polyethylene Polypropylene Polystyrene
Large Housings and Hollow Shapes	
 Boat hulls, shrouds for motorcycles and agricultural equipment, housings for large appliances, pressure vessels, tanks, tubs, ducts	ABS* HD Polyethylene* Phenylene oxide* Polyester* (TP) Polyester/glass (TS) Polypropylene* Polystyrene* Polyurethane* PVC* *Often in structural foam
Optical or Transparent Parts	
Optical lenses and fibers, taillight lenses, safety glazing, refrigerator shelves	Acrylic Cellulose butyrate Polycarbonate Polystyrene
Parts for Wear Applications	
Gears, bearings, wear strips, tracks, chute liners, roll covers, industrial tires	Acetal Fluoroplastics Nylon Phenolic Polyester (TP) Polyimide Polyurethane UHMW Polyethylene

TP = Thermoplastic, TS = Thermoset

The selection of plastics requires a great deal of experience. There is no simple procedure. Any new application of a plastic should be tested under real-use conditions encompassing appropriate combinations of heat, cold, chemicals and weathering. To make a first "ball park" selection the chart to the left might be used.

The following brief summaries further highlight the properties and characteristics of the most common families of plastics. Only families are mentioned; family properties can be changed by using fillers, plasticizers or reinforcements.

A quick guide to thermoplastics

Thermoplastics generally offer higher impact strength, easier processing, and better adaptability to complex designs than do thermosets. For more detailed information, consult the chapters that follow.

ABS (acrylonitrile-butadiene-styrene): Very tough, yet hard and rigid; fair chemical resistance; low water absorption, hence good dimensional stability; high abrasion resistance; easily electroplated.

Acetal: Very strong, stiff engineering plastic with exceptional dimensional stability and resistance to vibration fatigue; low coefficient of friction; high resistance to abrasion and chemicals; retains most properties when immersed in hot water.

Acrylic: High optical clarity; excellent resistance to outdoor weathering; hard, glossy surface; excellent electrical properties; fair chemical resistance; available in brilliant, transparent colors.

Cellulosics: Family of tough, hard materials: cellulose acetate, propionate, butyrate, and ethyl cellulose. Property ranges are broad because of compounding; available with various degrees of weather, moisture, and chemical resistance; fair to poor dimensional stability; brilliant colors.

Fluoroplastics: Large family (PTFE, FEP, PFA, CTFE, ECTFE, ETFE, and PVF_2) of materials characterized by excellent electrical and chemical resistance, low friction, and outstanding stability at high temperatures; strength is low to moderate; cost is high.

Nylon (polyamide): Outstanding toughness and wear resistance; low coefficient of friction; excellent electrical properties and chemical resistance; generally poor dimensional stability (varies among different types, however).

Phenylene Oxide: Excellent dimensional stability (very low moisture absorption); superior mechanical and electrical properties over a wide temperature range. Resists most chemicals but is attacked by some hydrocarbons.

Polycarbonate: Highest impact resistance of any rigid, transparent plastic; excellent outdoor stability and resistance to creep under load; fair chemical resistance; some aromatic solvents cause stress cracking.

Polyester: Excellent dimensional stability, electrical properties, toughness, and chemical resistance, except to strong acids or bases; notch sensitive; not suitable for outdoor use or for continuous service in water over 125 F; also available in thermosetting formulations.

Polyethylene: Wide variety of grades: low, medium, and high density formulations. LD types are flexible and tough. MD and HD types are stronger, harder, and more rigid; all are lightweight, easy to process, low-cost materials; poor dimensional stability and heat resistance, excellent chemical resistance and electrical properties.

Polyimide: Outstanding resistance to heat (500 F continuous, 900 F intermittent) and to heat aging. High impact strength and wear resistance; low coefficient of thermal expansion; difficult to process by conventional methods; high cost.

Polyphenylene Sulfide: Outstanding chemical and heat resistance (450 F continuous); excellent low temperature strength; inert to most chemicals over a wide temperature range; inherently flame-retardant; requires high processing temperature.

Polypropylene: Outstanding resistance to flex and stress cracking; excellent chemical resistance and electrical properties; good impact strength above 15 F; good thermal stability below 225 F; light weight, low cost, can be electroplated.

Polystyrene: Low cost, easy to process, rigid, crystal-clear, brittle material; low heat resistance, poor outdoor stability; often modified to improve heat or impact resistance.

Polysulfone: Highest heat-deflection temperature of melt-processable thermoplastics; requires high processing temperature; tough (but notch-sensitive), strong, and stiff; excellent electrical properties, even at high temperature; can be electroplated; high cost.

Polyurethane: Tough, extremely abrasion and impact resistant material; good electrical properties and chemical resistance; can be made in solid moldings or flexible foams; UV exposure produces brittleness, lower properties, and yellowing; also made in thermoset formulations.

Polyvinyl Chloride: Many formulations available, but most are classed as either rigid or flexible; rigid grades are hard, tough, and have excellent electrical properties, outdoor stability, and resistance to moisture; flexible grades (containing plasticizer) are easier to process but have lower properties; heat resistance is low to moderate for most types of PVC; low cost.

A quick guide to thermosets

In general, thermosets have better dimensional stability, heat resistance, chemical resistance and electrical properties than do the thermoplastics. Most thermosets are used principally in filled and/or reinforced form to increase dimensional stability or other properties, or for economy. Most formulations require heat and/or pressure for curing. For more detailed information consult the chapters that follow.

Alkyd: Easier, faster to mold than most thermosets; no volatile byproducts.

Allylic (diallyl phthalate): Outstanding dimensional stability and electrical properties; easy to mold, excellent resistance to moisture, chemicals, and liquid oxygen at high temperatures.

Aminos (urea, melamine): Abrasion and chip resistant; good solvent resistance; urea molds faster and costs less; melamine has harder surface and higher heat and chemical resistance.

Epoxy: Exceptional mechanical strength, electrical properties, and adhesion to most materials; some formulations can be cured without heat or pressure.

Phenolic: Low-cost material with good balance of mechanical, electrical, and thermal properties; limited in color to black and brown.

Polyester: Excellent balance of properties, unlimited colors, transparent or opaque, gives off no volatiles during curing; widely used with glass reinforcement to produce "fiberglass" boat hulls, automobile body panels, and other high-strength components; also available in thermoplastic formulations.

Polyurethane: Can be flexible or rigid, depending on formulation; outstanding toughness and resistance to abrasion and impact; particularly suitable for large foamed parts, in either rigid or flexible types; also produced in thermoplastic formulations.

Silicone: Outstanding heat resistance (from −100 to +500 F), electrical properties, and compatibility with body tissue; cures by a variety of mechanisms, high cost; available in many forms laminating resins, molding resins (rigid and flexible), coatings, casting or potting resins, and sealants.

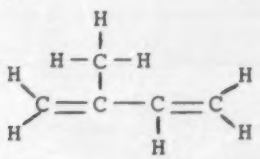
SECTION 3: ELASTOMERS

Materials that recover their original dimensions after being deformed are called elastomers. These have polymeric chains which are deformed when a stress is applied. When the stress is removed, the chains return to their original forms. The most common elastomer is rubber. There are several types of rubbers, and each type can be modified by various chemical processes. The hardness and elasticity of rubber can be modified by cross-linking with oxygen or sulfur. This process is called vulcanizing. The more cross-links, the harder the rubber. Accelerators and activators, such as fatty acids, increase the number of cross-links and speed vulcanization.

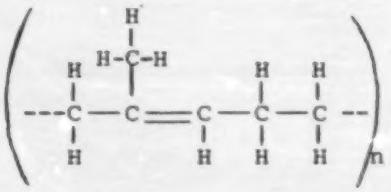
Normal Stressed Stress Removed

Fillers, such as carbon black, clay or fibers are used to change mechanical properties such as tensile strength and abrasion resistance. Oxidation retarders are added to rubber to prevent aging and cracking. Plasticizers, such as oils, tars and other petroleum products, are added to rubber to preserve its plasticity during molding and extruding processes.

Natural rubber is a resin from plants and trees that grow in tropical climates. Natural rubber is a polyisoprene. The rubber hardens when vulcanized with 30% sulfur; then it is cured and neutralized with magnesium carbonate. Carbon black is added to provide strength. The letter "n" used below stands for any positive whole number.

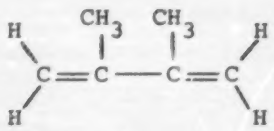


isoprene monomer

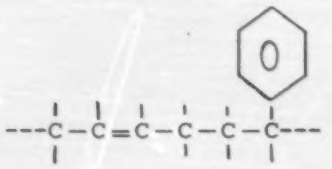


polyisoprene

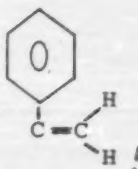
Styrene-butadiene rubber (SBR) is the most common synthetic elastomer. The polymer is about 80% butadiene and 20% styrene. It may be polymerized cold or hot.



Butadiene



SBR

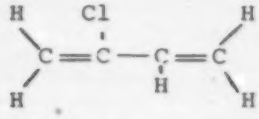


Styrene

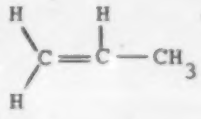
The cold polymerized material is used for automobile tires. There are many types of synthetic elastomers, each made with one or two monomers.

Student Problem

1. Draw the chemical structure of polychloroprene rubber, and of polyisopropylene rubber.



Chloroprene



Isopropylene

With the wide range of elastomers available, it is important to know how to specify the exact material needed. ASTM has developed a classification system (ASTM D1418) which designates elastomers with letters. The "R" class has an unsaturated carbon chain: for example natural rubber is designated "NR". The "M" class has a saturated chain of the polymethylene type. The "Q" class contains the silicone based rubbers. The "U" class contains those rubbers with carbon, oxygen and nitrogen in the polymer chain.

A related method to classify rubbers is the ASE-ASTM system which designates type R rubber as the non-oil resistant rubber and type S rubber as the oil-resistant synthetic rubber. This is an older system, but still in use.

Most rubbers, natural and synthetic, are classified as thermoset elastomers because they are vulcanized in a mold and they cannot be easily remolded. The properties of some thermoset elastomers are tabulated below.

Typical properties of thermoset elastomers

	Natural rubber	Polyiso-prene	Styrene butadiene	Butadiene	Isobutene isoprene	Chlorinated isobutene isoprene	Ethylene propylene copolymer	Chloroprene (neoprene)	Polyacrylate	Silicone	Urethane	Fluoro-silicone	Fluorocarbon
ASTM D1418 designation →	NR	IR	SBR	BR	IIR	CIIR	EPM	CR	ACM	MQ, PMQ, VMQ, PVMQ	AU, EU	FVMQ	FKM
ASTM D2000/SAE J200 type, class →	AA	AA	AA, BA	AA	AA, BA	AA, BA	AA, BA, CA	BC, BE	DF, DH	FC, FE, GE	BG	FK	HK
Specific gravity, base polymer	0.92	0.91	0.94	0.91	0.92	0.92	0.86	1.24	1.09	0.96	1.05-1.30	0.98	1.85
Tensile strength, max, reinf (psi)	4,000	4,000	3,500	3,000	3,000	3,000	3,000	4,000	2,500	1,200	10,000	1,200	2,500
Elongation, max, reinf (%)	700	700	600	600	800	700	600	600	400	700	700	400	300
Hardness, Shore A	30-90	30-90	40-90	40-80	40-80	40-80	30-90	30-90	40-85	30-85	40-100	60-80	60-95
Brittle point (F)	−80	−80	−80	−100	−80	−80	−90	−80	−40	−90 to −180	−60 to −90	−85	−40
Resilience at 73 F	A	A	B	A	D	C	B	B-A	C	D-A	C-A	C	C
Compression set	A	A	A	B	C-B	B-A	A	B-A	B	C-A	D-A	B	B-A
Electrical properties	A	A	A	A	A	A	A	A	C	B-A	B	A	B
Adhesion to metal	A	A	A	A	C-A	C-A	C-B	B-A	B	B	C-B	C	C
Resistance to:													
Tearing	A	A	C	C	B	B	C	C-B	D-C	D-C	A	D	C-B
Abrasion	A	A-B	A	A	C	C	B	A	C	D-C	A	D	B
Flame	D	D	D	D	D	D	D	B-A	D	C-A	D-A	A	A
Ozone	NR	NR	NR	NR	A	A	A	A	A	A	A	A	A
Weather	D	D	D	D	A	A	A	A	A	A	A	A	A
Oxidation	B	B	C	C	A	A	A	A	B	A	B	A	A
Water	A	A	B-A	B	C-A	B-A	A	B	D	B-A	D-C	A	A
Steam	C	C	C	C	C-A	B-A	B-A	C	NR	C-B	D	C-B	B
Acids (dilute/conc)	A/C-B	A/C-B	C-B/C-B	C-B/C-B	A/A	A/A	A/A	A/A	D-C/D-C	B/C	C/D	A/B	A/A
Alkalies (dilute/conc)	A/C-B	A/C-B	C-B/C-B	C-B/C-B	A/A	A/A	A/A	A/A	D-C/D-C	A/A	C/D	A/B	A/A
Synthetic lubricants	NR	NR	NR	NR	NR	NR	NR	D	D	NR	D	A	A
Lubricating oils (high aniline/low aniline)	NR/NR	NR/NR	NR/NR	NR/NR	NR/NR	NR/NR	NR/NR	A/B	A/A	B/C	A/B	A/A	A/A
Animal, vegetable oils	D-B	D-B	D-B	D-B	B-A	B-A	B-A	B	B	A	A	A	A
Aliphatic hydrocarbons	NR	NR	NR	NR	NR	NR	NR	C	B	NR	B	A	A
Aromatic hydrocarbons	NR	NR	NR	NR	NR	NR	NR	D	D	NR	C	A	A
Gas permeability	C	C	C	C	A	A	C	B	B	D	D	D	A

A = Excellent, B = Good, C = Fair, D = Use with caution, NR = Not recommended

Thermoplastic elastomers have similar properties as the thermoset (or vulcanized) elastomers. Thermoplastic elastomers are fabricated on standard plastic molding equipment. The principal thermoplastics are polyester copolymers, styrene-butadiene block copolymers and polyurethane elastomers. The abrasion resistance of polyurethane materials is outstanding among elastomers; also their low temperature flexibility and oil resistance are good. Urethane tubing is used for fuel lines, hydraulic devices and parts requiring oxygen and ozone resistance.

SECTION 4: ADHESIVES

An adhesive is any substance capable of holding materials together by surface attachment. Adhesives are applied to surfaces, and objects joined by adhesives are notably free from any residual stresses. The major disadvantage of adhesives is that most are organic materials and cannot be used at extreme temperatures.

Adhesion is an attraction between unlike materials. Cohesion is the attraction of a material for itself. Failure in an adhesive bond may occur with the adhesive itself (cohesive failure), or it may occur at the material-adhesive interface (adhesive failure). Most failures are adhesive, and are caused by poor surface preparation of the materials to be joined. Surface cleanliness is very important.

The materials which are to be joined together by an adhesive are called the adherends. Tackiness is that property of an adhesive which causes it to stick to a surface. The conversion of a tacky adhesive to a solid is called setting or curing. Wettability refers to the spreading of an adhesive over the surface of a material. Any thick, tacky viscous liquid is called a resin.

Most adhesives are polymers which can be divided into thermoplastics, thermosets and elastomers. As with plastics, the thermosets are the most stable and strong.

The method of curing serves as a method for classification of adhesives. Solvent release types cure by the escape of solvents, and they are therefore limited to applications in which at least one of the bonded surfaces is porous enough to allow the escape of solvent vapor. The dispersion types like "Elmer's Glue" are emulsions of thermoplastics in water, and they cure through solvent release. Cold setting types of adhesives (i.e. household epoxide) are generally low molecular weight thermosets which set to a hard solid when mixed with a catalyst before application. Hot setting types are similar to cold setting types but require heating to produce cross-linking; they are usually much stronger than the cold setting types. Vulcanization types of adhesives are elastomers. Hot-melt adhesives are thermoplastics which are liquified by heat before they are applied. The following table lists the properties of several types of adhesives.

Structural Adhesives: What they are and what they can do

HOT-MELT ADHESIVES

Thermoplastic resins — 100% solids
Fast application and fast set
Rigid to flexible bonds
Bonds to permeable or impermeable surfaces
Nonpolar, adhesion poor and wetting poor
Low cost in materials and labor
Requires special dispensing equipment
Insensitive to moisture and solvent attack
Low heat resistance — degrades as temperatures rise
Poor creep resistance — 5 psi at 125 F

DISPERSION OR SOLUTION ADHESIVES

Thermoplastic resins—20 to 50% solids
Very easy to apply—long shelf life
Slow or fast setting by evaporation
Low material cost and solvent loss
Excellent wetting and penetration
No special equipment required
Moderate clamp pressure needed
Low strength under load poor creep resistance
Requires two permeable surfaces
Sensitive to heat, solvent, and moisture

SILICONE ADHESIVES

Thermoset—100% solids—liquid
Rubber like—high impact and peel strength
Retains properties in 100 to 400 F temperature range
Excellent sealant for low stress applications
One component—short shelf life
Easy application—1 to 5-day cure
Resists most chemicals and solvents
Simple equipment needed
Reversion possible
High material cost

CYANOACRYLATE ADHESIVES

Thermosetting—100% solids—liquid
Easiest to apply and cure
Fast cure—30 secs. to 5 mins.
Low viscosity—mated surfaces needed
Good tensile strength—poor impact strength
No special equipment needed
Will not bond permeable materials
High material cost—poor shelf life
Poor solvent resistance
Handling hazards—bonds to skin

"SECOND-GENERATION" MODIFIED ACRYLIC ADHESIVES

Thermoset-100% reactive — liquids and pastes
Fast room-temperature cure—3 to 60 sec
One or two pack
High strength bonds with metal and plastics—good peel and shear strength
Tolerant of dirty surfaces
Good gap filling properties
Limited open time
Versatile application techniques
Variable curing time and pot life
Excellent for engineered and reinforced plastics
Characteristic acrylic odor
Rigid and flexible bonds are possible

PHENOLIC OR UREA ADHESIVES

Thermoset resins—100% solids or solution
Gases during cure—(solvent evaporates)
High tensile strength—low impact strength
Highly polar—excellent adhesion
Long shelf life—application easy
Requires high pressure—oven cure
Very low material cost
Excellent wetting and penetration
High shrinkage stresses—brittle

EXPOXY ADHESIVES

Thermoset—100% solids—liquid
Variable pot life and cure time
Long shelf life—one to two components
Rigid or flexible bonds—highly polar
Poor creep under load—little shrinkage
Resists most chemicals and solvents
Wide variety of formulations available
Requires careful controls and clean surfaces
Need equipment to weigh, mix, dispense, and clamp
Requires clean surfaces

POLYURETHANE ADHESIVES

Thermoset—100% solids—liquid
Flexible sealant/adhesive—low creep
Bonds permeable or impermeable surfaces
One or two components—room or oven cure
Good flexibility at low temperature
Sensitive to moisture both when unmixed or cured
May undergo reversion with heat and moisture
Moderate material cost
Some formulations are toxic
Special equipment to mix and dispense dispense

ANAEROBIC ADHESIVES

Thermoset—100% solids—liquid
One component—moderate cost
Easiest application—simple cure
Machinery and structural grades available
Good cohesive, but low-adhesive strength
Excellent for bolts, nuts, and static joints
Requires primer for many materials
Not suitable for permeable surfaces
Will not cure where air contacts
Crazes some plastics

INDEX

Acidic, 6
Adhesive, 56
Alloy, 1
Anions, 19
Anode, 19
Anodizing, 35
Autoionization, 5
Avogadro's Law, 39

Barometer, 37
Basic, 6
Battery, lead storage, 28
Boyle's Law, 38

Cathode, 19
Cathodic protection, 25
Cations, 19
Cell:
    concentration, 22
    dry, 28
    electrochemical, 29
    fuel, 29
    half, 19, 28
Charles' Law, 39
Cohesion, 56
Conservation of Matter Law, 8
Copolymer, 49
Corrosion, galvanic, 23
Corrosion inhibitor, 34
Crosslinking, 49
Crystalline plastics, 47
Crystallinity, 47
Curing, 45, 56

Dalton's Law, 42
Dehumification, 34
Dezincification, 26

Elastomers, 53
Electrodes, 19
Electrolysis, 29
Electrolyte, 19, 29
Electroplating, 32
Equations, balancing, 13

Faraday's Law, 30

Galvanic cell, 19
Galvanization, 25, 33
Gas law constant, 40
Graham's Law, 43
Gram molecular weight, 14

Ideal gas, 38
Ideal Gas Law, 40
Ion-electron method, 11
Ion product, 13

Molality, 2
Molarity, 2
Mole, 14
Mole fraction, 2

Normality, 3

Oxidation numbers, 9

Passivation, 35
pH, 5
Plastic, 45
Plasticizers, 53
Polymer, 45
ppm, 2
Pressure, 36
   absolute, 36
   gauge, 36

Reduction-oxidation reactions, 9
Resin, 56
Rubber, 53

Solute, 1
Solution, 1
Solvent, 1
Stoichiometry, 13
STP, 39

Tackiness, 56
Thermoplastics, 45
Thermoset,
elastomers, 54

Vapor pressure, 42
Vulcanization, 53

Wettability, 56